THE NAPHTHALENE SENSITIZED PHOTORACEMIZATION OF SULFOXIDES

Thesis by

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Facts are stubborn things.

Alain René Le Sage

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ABSTRACT

The sensitized photoracemization of alkyl aryl sulfoxides has been shown to result from energy transfer from the singlet state of naphthalene. The possibility of exothermic electronic energy transfer has been ruled out on the basis of spectroscopic data. It is postulated that an exciplex is reversibly formed from an excited singlet state naphthalene molecule and a ground state molecule of the sulfoxide. This excited complex then undergoes radiationless decay converting electronic energy to vibrational energy partitioned between the two components of the exciplex. Enough vibrational energy appears in the aryl sulfinyl center to effect thermal pyramidal inversion with high efficiency. Steric and electronic effects on the rates of fluorescence quenching or of photoracemization are small.

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INTRODUCTION

The nature of the sulfoxide functional group, R-SO-R', has been of interest to physical and organic chemists for almost forty-five years. With the increasing sophistication of research tools the answers to questions of bonding, structure and reactivity are being refined, however, many problems remain unsolved.

Bonding and Structure of Sulfoxides

Dipole measurements by Bergmann and Tschudnowsky (1) and Hampson, Farmer and Sutton (2) showed that the three groups bonded to sulfur are not coplanar. In fact, estimates of the valency angles were about 115°, so that sulfoxides must have pyramidal geometry.

Even now the bonding of sulfur to oxygen remains in controversy. Measurements of the molecular parachors (3) and the dipole moment of the S-O bond (4) indicated that it is largely semipolar in nature. Such a formulation places a positive charge on sulfur and a negative charge on oxygen. Results of infrared group frequency studies (5) and comparison of ^{13}C-H coupling constants (6) showed that the S-O link approximates a covalent double bond with only a small amount of polar character. This model makes use of the 3 d-orbitals of sulfur in an expansion of the valence shell.

Koch (7) has treated the bonding in sulfones in some

detail, and his arguments may be extended to sulfoxides (8). Tetrahedral geometry is assumed with oxygen, the two organic radicals and the lone electron pair at the corners of and sulfur in the center of a tetrahedron. The internuclear axis between sulfur and oxygen is oriented along the z-axis in the coordinate system, so that the p_x- and p_y-orbitals of oxygen may interact favorably with the d_{xz}- and d_{yz}-orbitals of sulfur. The overlap may be interpreted as a partial triple bond. It should be noted that fixing the coordinates for maximum overlap in the S-O link precludes optimal overlap of the sulfur d-orbitals with p-orbitals of any of the attached R groups. However, some overlap is possible whatever the orientation of the organic group, so that conjugation is not a sensitive function of steric limitations.

Resolution of Dissymmetric Sulfoxides

If sulfoxides possess pyramidal geometry and rapid pyramidal inversion does not occur at room temperature, then it should be possible to demonstrate the presence of enantiomeric forms in suitably substituted compounds, that is where $R \neq R'$ in R-SO-R'. This was accomplished first by Harrison, Kenyon and Phillips (9) who were able to resolve 4'-amino-4-methyldiphenyl sulfoxide by fractional crystallization of the diastereomeric salt formed with d-camphorsulfonic acid. Since that time a number of

procedures (10) have been employed in the syntheses of optically active sulfoxides. Sulfoxides of low optical purity have been produced by the oxidation of sulfides with optically active peracids (11,12,13,14,15) or by the reduction of racemic sulfoxides with optically active thiols (16). Somewhat higher optical purity was obtained in the oxidation of sulfides in growing aerobic cultures of Asperillus niger (17, 18). A more general synthetic approach involving the resolution of a menthyl sulfinate followed by treatment with a Grignard reagent has been developed by Andersen (19, 20) and others (21, 22). More recently a procedure for the resolution of racemic sulfoxides by treatment with an optically active platinum complex has been developed by Cope (23).

Catalyzed and Thermal Racemization of Sulfoxides

With a number of procedures available for the preparation of sulfoxides of high optical purity, much of the research on sulfoxides has been directed toward the study of mechanisms of racemization of these compounds. The racemization of sulfoxides may be catalyzed with sulfuric acid (24), phosphoric acid (25), acetic, chloroacetic or trifluoroacetic acids (26, 27), hydrogen chloride in organic solvents (28), nitrogen tetroxide (29), charcoal (30) and methyl lithium (31). Inversion of sulfoxides may be accomplished by treatment with triethyloxonium

fluoroborate followed by aqueous base (32, 33).

More pertinant to the photoracemization of sulfoxides are studies on the mechanisms of thermal racemization. Racemization of benzyl p-tolyl sulfoxide proceeds (34) by a radical dissociation-recombination mechanism. Allylic sulfoxides are racemized by a mechanism involving a concerted sulfoxide-sulfenate interconversion (35). Aside from these special cases, the thermal racemization of sulfoxides appears to proceed by a pyramidal inversion which involves molecular vibration without carbon-sulfur bond cleavage (36). This process is easily studied at temperatures around 200°. For alkyl aryl and diaryl sulfoxides activation energies of 36-43 kcal $mole^{-1}$ and entropies of activation in the range -8 to 4 cal $°K^{-1}$ $mole^{-1}$ have been measured.

Photochemistry of Sulfoxides

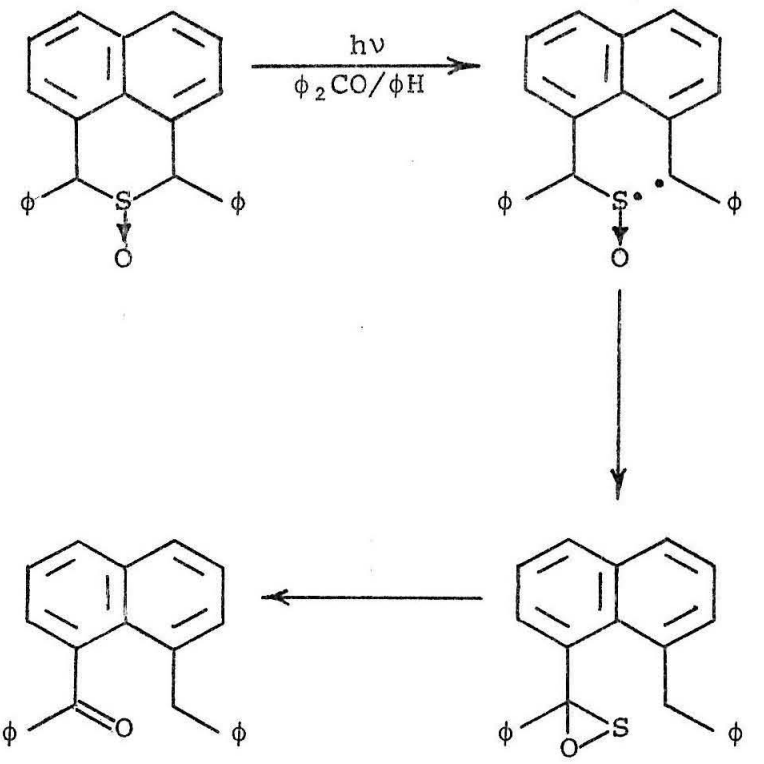
The photochemistry of sulfoxides has received very little attention from investigators of these compounds. For this reason, little is known about the general effects of light on the R-SO-R' functional group. However, the work cited below indicates some of the photoreactions which may be expected.

Schenck and Krauch (37) have investigated the photochemistry of diethyl and dimethyl sulfoxides in the presence of oxygen and suitable sensitizers. When

solutions of dimethyl sulfoxide and dye sensitizers such as Bengal rose, chlorophyll or methylene blue in the presence of oxygen were irradiated with light absorbed by the dye, dimethyl sulfone was produced in 94-99% yield based on the oxygen consumed. Similar irradiations under an argon blanket led to no reaction. Direct irradiation in the quartz ultraviolet of dimethyl sulfoxide under an argon blanket gave traces of dimethyl sulfide and dimethyl sulfone. The dye sensitized reaction is probably the result of attack of singlet oxygen produced by energy transfer. The photodisproportionation reaction has been observed in a number of investigations, but detailed studies have never been undertaken.

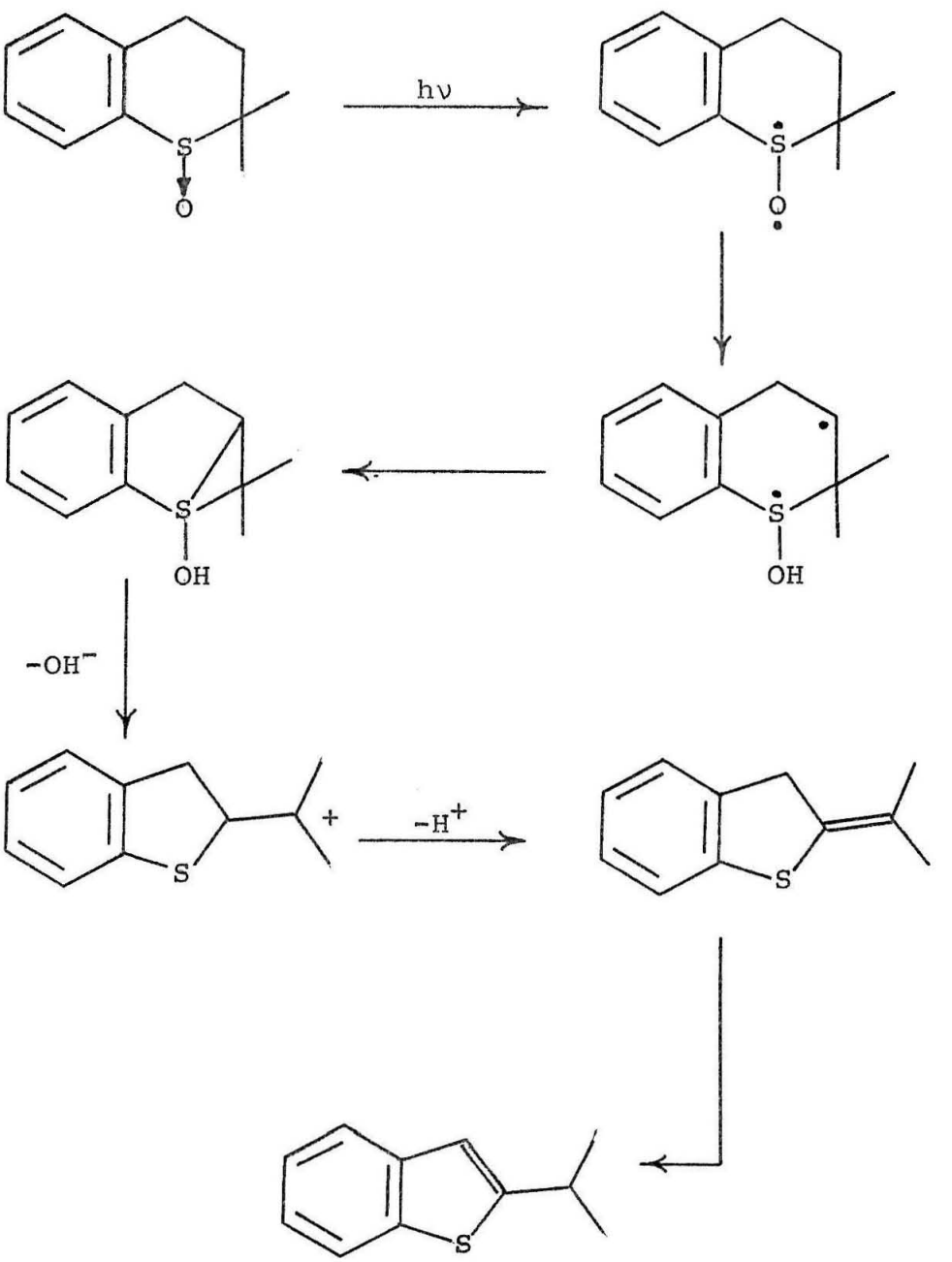
Schultz, DeBoer and Schlessinger (38) have recently observed the photodesulfurization of a sulfoxide. The sensitized conversion of cis- or trans-1,3-dihydro-1,3-diphenyl-2-thiaphenalene 2-oxide to 1-benzoyl-8-benzylnaphthalene probably proceeds in the manner shown in Scheme I. The possible pyramidal inversion of the compound was not studied although the authors indicate that no epimerization was observed.

Scheme I



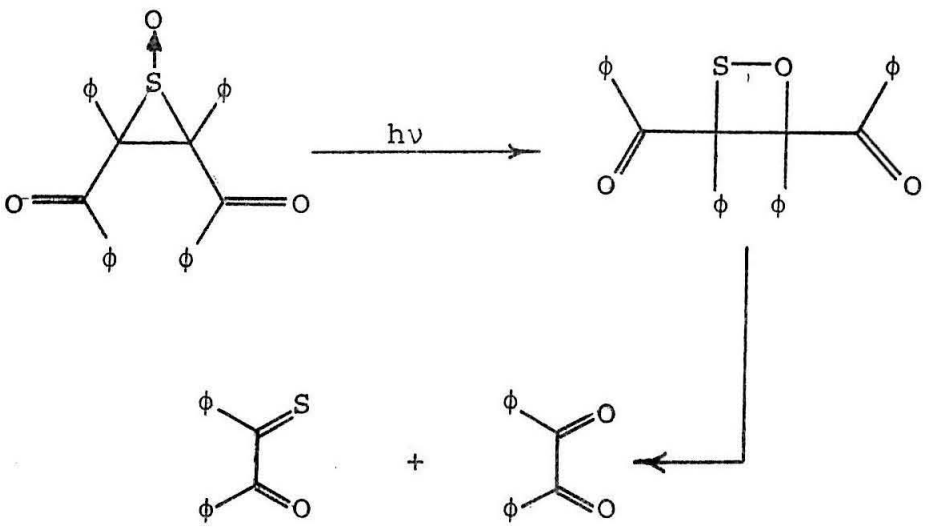
Archer and Kitchell (39)have observed that upon direct irradiation 2,2-dimethylthiachroman 1-oxide is converted to 2-isopropylbenzothiaphene. They postulated that this dehydrative photorearrangement proceeds as shown in Scheme II.

Scheme II



Dittmer, Levy and Kuhlmann (40) have observed the photochemical conversion of dibenzoylstilbene episulfoxide to a mixture of monothiobenzil and benzil. A reasonable mechanism for this reaction is shown in Scheme III.

Scheme III



Hammond, Mislow and their coworkers (41, 42) first investigated the photoracemization of sulfoxides. They observed that upon direct irradiation diaryl and aryl alkyl sulfoxides were racemized with some concurrent decomposition. In the case of dialkyl sulfoxides only decomposition was observed. With naphthalene both intra- and intermolecular

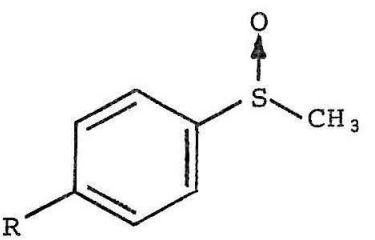
sensitization of the photoracemization of alkyl aryl sulfoxides were demonstrated. Attempts to show naphthalene sensitization of the inversion of dialkyl sulfoxides were unsuccessful. The sensitized photoracemization was studied in some detail employing piperylene as a triplet quencher of naphthalene. Although a high concentration of piperylene was required to completely quench the racemization, it was postulated that the intermolecular sensitization might involve triplet energy transfer exclusively. In the case of the intramolecular sensitization by the naphthalene chromophore the authors suggested that a weak coupling exists between the non-conjugated naphthalene and aryl sulfinyl moieties. It was postulated that the delocalized triplet state is capable of undergoing racemization. Further studies of the naphthalene sensitized photoracemization of alkyl aryl sulfoxides have been undertaken (43) and are presented below.

RESULTS AND DISCUSSION

Several preliminary studies on the system in which the photoracemization of alkyl aryl sulfoxides is effected by the use of naphthalene as a sensitizer cast serious doubt on the conclusions reached by Mislow and Hammond (41, 42) and led to a rather different rationalization of the phenomenon.

Assignment of Singlet State Energy Levels of Sulfoxides

Of first interest was the determination of the energies of the excited singlet and triplet states of the sulfoxides. Some work on the assignment of states from the absorption spectra existed in the literature (44, 45, 46, 47), and the following discussion is based on this. The absorption spectrum of (±)-methyl p-tolyl sulfoxide, 1a,



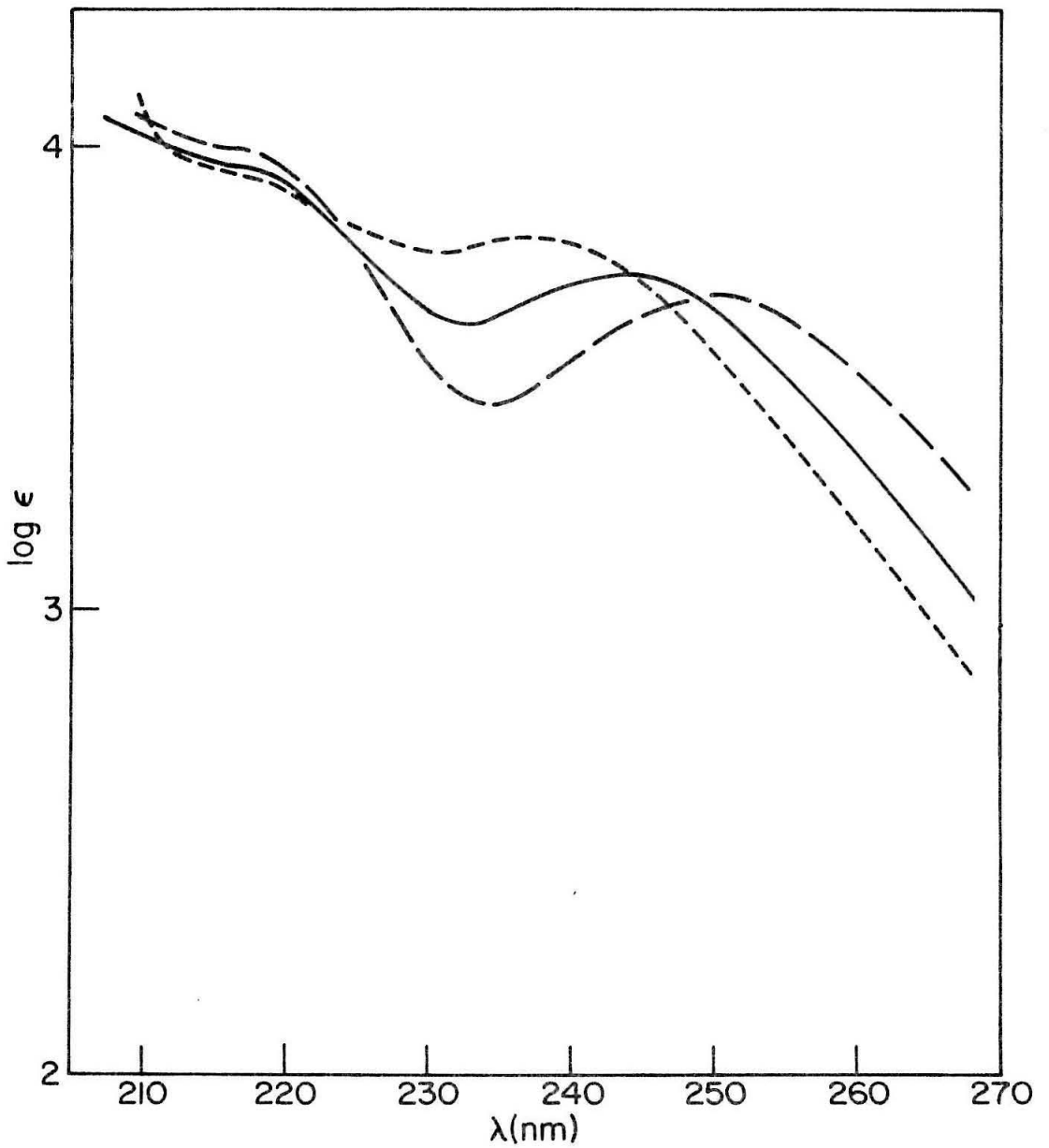
1a R = CH_3 d R = OH

b R = Br e R = H

c R = Cl f R = $C(CH_3)_3$

in several solvents are shown in Figure 1. The spectra of the other para-substituted alkyl aryl sulfoxides are very similar. A short wavelength transition appears as a shoulder in the region of 217.5 nm. From the position, intensity and lack of solvent dependence of this transition it may be assigned as a localized ^1L_a band of the aromatic ring. Assignment of the long wavelength absorption at about 243 nm is more difficult. Jaffé and Orchin (47) refer to this as the ^1L_b band of benzene which has been considerably perturbed by resonance interaction with the sulfinyl group. They view this perturbation as arising from donation of the sulfur lone pair into an unoccupied orbital of benzene and from donation of electrons from the aromatic system into the vacant $d\pi$-orbital of the sulfur atom. However, in ethanol the long wavelength absorption of methyl phenyl sulfoxide splits into two bands (44). Therefore, an assignment of the transition at 243 nm as a superposition of the ^1L_b band of benzene and the $\pi^* \leftarrow n$ band of the sulfinyl group is equally reasonable. The transition in dialkyl sulfoxides corresponding to excitation of one of the sulfur lone pair electrons into the sulfur-oxygen π-system is found at about 220 nm depending on the polarity of the solvent, and a red shift of 20 nm due to conjugation with the aromatic system does not seem unreasonable (47). If the ^1L_b band of benzene is hidden under

Figure 1. Absorption spectra of (±)-methyl p-tolyl sulfoxide, 1a, in various solvents: — — — in cyclohexane, ———— in acetonitrile, --------- in ethanol.


log ε
4
3
2
210
220
230
240
250
260
270
λ(nm)

this stronger transition, the observed solvent dependence would be expected.

The fact that the long wavelength transition in these sulfoxides is broad and possesses no vibrational fine structure makes the assignment of the energy level in the first excited singlet state difficult. This level is placed at approximately 102 kcal $mole^{-1}$, which would correspond to a 0-0' band at 280 nm if one were observable. Since the first excited singlet state of naphthalene lies at about 90 kcal $mole^{-1}$, electronic energy transfer from this state of naphthalene to the singlet state of the sulfoxides is endothermic by 12 kcal $mole^{-1}$ and would not be expected to occur at any appreciable rate.

Assignment of Triplet State Energy of Sulfoxides

The triplet state of naphthalene lies at about 60.9 kcal $mole^{-1}$. If the long wavelength band of the sulfoxides corresponds to a superposition of the $\pi^* \leftarrow n$ band of the sulfinyl group and the ^1L_b band of benzene, the lowest triplet state in these compounds is probably benzene-like. It seems unreasonable that the singlet-triplet splitting in sulfinyl $\pi^* \leftarrow n$ states is much larger than in ketones.

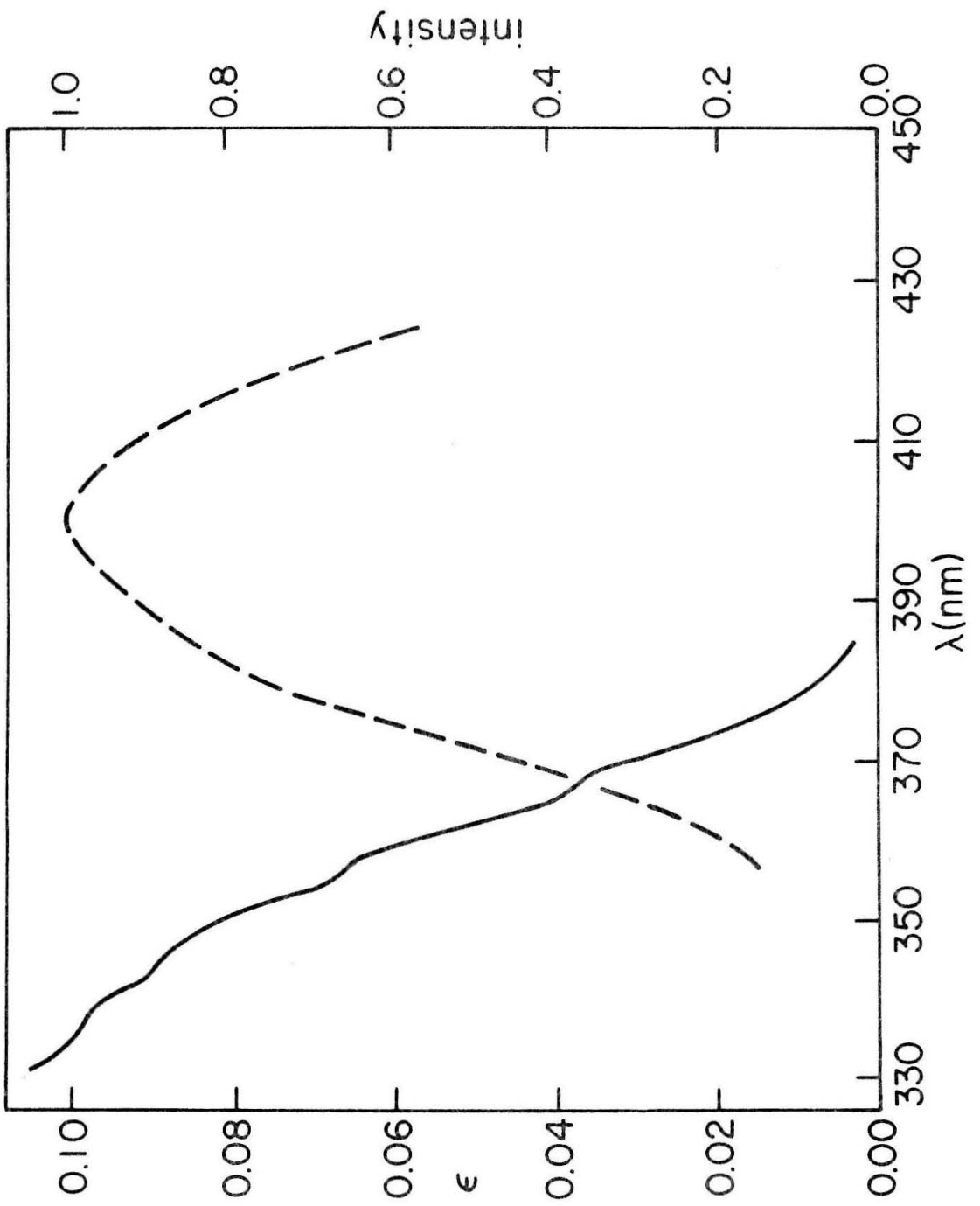
The approximate triplet state energy of (±)-methyl p-bromophenyl sulfoxide, 1b, was determined by comparison of the phosphorescence and singlet-triplet absorption spectra. In an ether--alcohol glass at 77°K (1:2 by

volume) this compound shows weak and structureless long-lived emission. In chloroform solution (±)-methyl p-bromophenyl sulfoxide, 1b, carefully purified by recrystallization, sublimation and zone refining, showed weak, slightly-structured absorption corresponding to the phosphorescence as shown in Figure 2. These results place the triplet state energy at about 79 kcal $mole^{-1}$, which is reasonable for a slightly perturbed benzene triplet level. This spectroscopic assignment indicates that transfer of triplet electronic excitation from naphthalene to the alkyl aryl sulfoxides should be extremely inefficient since the process is endothermic by about 18 kcal $mole^{-1}$.

Chemical Evidence Against Triplet Energy Transfer

Evidence will be presented which shows that the excited singlet state of naphthalene is involved in the transfer of energy to the sulfoxide. Therefore, the observation that triplet energy transfer from naphthalene to sulfoxide is endothermic by 18 kcal $mole^{-1}$ is not sufficient evidence to rule out the possibility of its occurance. Any participation of the triplet state of naphthalene was ruled out by double sensitization experiments. Degassed solutions of 0.05 M benzophenone, 0.03 M naphthalene and 0.05 M (+)-(R)-methyl p-chlorophenyl sulfoxide, 1c, or (+)-(R)-methyl p-bromophenyl sulfoxide, 1b, in

Figure 2. Triplet state spectra of (±)-methyl p-bromophenyl sulfoxide, 1b: ———— singlet-triplet absorption spectrum in chloroform, — — — phosphorescence spectrum in ether--alcohol glass at 77° K.


intensity
1.0
0.8
0.6
0.4
0.2
0.0
450
430
410
390
370
350
330
λ(nm)
ε
0.10
0.08
0.06
0.04
0.02
0.00

acetonitrile were irradiated at 366 nm where only benzophenone absorbs light. It is known that benzophenone undergoes intersystem crossing to the triplet state with unit efficiency and that the triplet state is readily photoreduced in any solvent containing abstractable hydrogens. This photoreduction may be quenched if energy transfer to a molecule with a lower energy triplet state occurs with high efficiency. Completely efficient transfer of triplet energy to naphthalene was demonstrated by the fact that no photoreduction of benzophenone occurred. The quantum yields of inversion of sulfoxide under these conditions were less than 1% of those observed when naphthalene was directly irradiated in the presence of sulfoxide and are within experimental error of zero.

Evidence Against a Ground State Complex

If a stable ground state complex between the sulfoxide and naphthalene were formed, it is conceivable that irradiation of this species would lead to stereomutation of the sulfoxide. The absorption spectrum of a mixture of naphthalene and (±)-methyl p-bromophenyl sulfoxide, 1b, showed no anomalous bands in the 240-350 nm region. If unlikely coincidences are ignored, the result implies that electronic interaction complexes between the two species do not have bound ground states.

Quantum Yield of the Disappearance of Sulfoxide

Mislow and Hammond (41, 42) report nearly quantitative recovery of sulfoxide in the naphthalene sensitized irradiations. It was of considerable importance to show that the rate of disappearance of sulfoxide was slow relative to the rate of racemization. First, this result would allow treatment of the inversion process as the only photochemical reaction in the mechanism. Second, by assuming that there was no destruction of sulfoxide the net rotations of the irradiated solutions could be directly related to the specific rotations of the partly racemized substrate. If sulfoxide were disappearing, it would have been necessary to isolate and purify this material from each sample tube in order to obtain quantitative data.

Prolonged irradiation of degassed solutions of 0.03 M naphthalene and 0.05-0.09 M (±)-methyl p-chlorophenyl sulfoxide, 1c, in acetonitrile led to disappearance of sulfoxide with a quantum yield less than 5% of that observed for the racemization under the same conditions. Fragmentary evidence obtained in prolonged irradiation of (±)-methyl p-bromophenyl sulfoxide, 1b, or (±)-methyl p-hydroxyphenyl sulfoxide, 1d, indicated that the corresponding sulfide is the only product. No sulfone, which is stable under the reaction conditions, was found in either case. Because of the inefficiency of this

process, the decomposition of sulfoxide was neglected in the kinetic analysis of the photoracemization.

The Proposed Mechanism for Intermolecular Sensitization

These observations limit the mechanisms to be considered for the sensitized racemization of alkyl aryl sulfoxides. Other results in the sensitized conversion of quadricyclene to norbornadiene (48, 49) and the asymmetric induction observed in the sensitized cis-trans isomerization of diphenylcyclopropane (48) suggested that the mechanism might depend upon activation of the substrate by the excited singlet state of the sensitizer as shown by the following equations.

$$N \xrightarrow{h\nu} N^1 \qquad (1)$$

$$N^1 \xrightarrow{k_f} N + h\nu' \qquad (2)$$

$$N^1 \xrightarrow{k_1} N \qquad (3)$$

$$N^1 \xrightarrow{k_{ic}} N^3 \qquad (4)$$

$$N^3 \xrightarrow{k_2} N \qquad (5)$$

$$N^1 + S(+) \underset{k_{-q}}{\overset{^{*}k_q}{\rightleftharpoons}} [N\cdot S(+)]^1 \qquad (6)$$

$$[N\cdot S(+)]^1 \xrightarrow{k(+)} N + S(+) \qquad (7)$$

$$[N\cdot S(+)]^1 \xrightarrow{k(-)} N + S(-) \qquad (8)$$

Step 1 shows the absorption of a photon by naphthalene. Steps 2 and 3 show decay of the excited singlet of naphthalene to the ground state either by the emission of a photon or by another first-order or pseudo first-order process. Steps 4 and 5 represent the intersystem crossing of the naphthalene singlet state to the triplet state and subsequent decay of the triplet to the ground state. These are the normal photophysical processes expected for an aromatic hydrocarbon.

The energy transfer process is represented by steps 6, 7 and 8. Step 6 shows the reversible formation of an excited state complex, or exciplex, in which a sharing of electronic energy between the sulfoxide and naphthalene occurs. Steps 7 and 8 show the radiationless decay of the exciplex in which vibrational energy is partitioned between the two partners. The vibrationally excited sulfoxide molecule may relax to sulfoxide with either the (+)-(R)- or (-)-(S)-configuration. Detailed consideration of these three steps as well as other possible mechanisms will be presented below.

By employing a steady state approximation for the concentration of the excited singlet state of naphthalene and for the concentration of the hypothetical exciplex the following kinetic laws are obtained. In these ex-

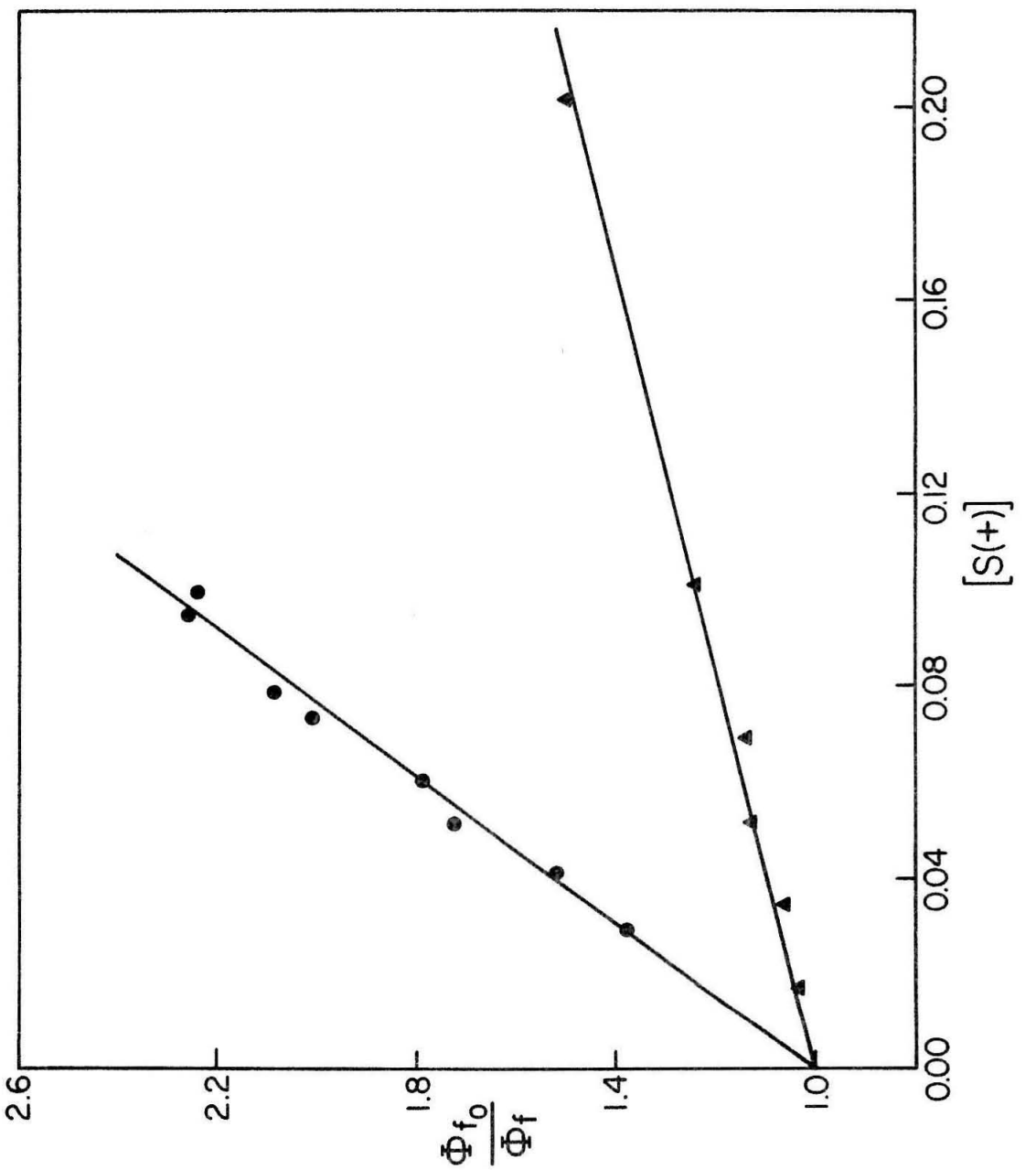
$$\frac{\Phi_{f_o}}{\Phi_f} = 1 + \frac{[k(+) + k(-)]\ k_q\ \tau_s\ [S(+)]}{k_{-q} + k(+) + k(-)} = 1 + k_Q\ \tau_s\ [S(+)]$$

$$\frac{1}{\Phi_{inv}} = \left(1 + \frac{1}{\tau_s\ k_Q\ [S(+)]}\right) \left(\frac{k(+) + k(-)}{k(-)}\right)$$

pressions Φ_{f_o} = quantum yield of naphthalene fluorescence in the absence of added quencher, Φ_f = quantum yield of naphthalene fluorescence with added sulfoxide, Φ_{inv} = quantum yield of inversion of the sulfoxide, τ_s = singlet lifetime of naphthalene, 78 ± 5 nsec for 0.03 M naphthalene in acetonitrile, and $k_Q = [k(+) + k(-)]\ k_q / [k_{-q} + k(+) + k(-)]$.

A test of the mechanism is provided by correlation of the rate of inversion with the quenching of the naphthalene fluorescence. Experiments were performed in which either the intensity or lifetime of the fluorescence from 0.03 M naphthalene in degassed acetonitrile was measured as a function of sulfoxide concentration. Representative data for (±)- or (+)-(R)-methyl p-tolyl sulfoxide, 1a, and (±)- or (+)-(R)-methyl p-chlorophenyl sulfoxide, 1c, are shown in Figure 3. The quantum yield

Figure 3. Quenching of naphthalene fluorescence by sulfoxides: ● methyl p-chlorophenyl sulfoxide, 1c, ▲ methyl p-tolyl sulfoxide, 1a.


2.6
2.2
1.8
1.4
1.0
$\frac{\Phi f_0}{\Phi f}$
0.00
0.04
0.08
0.12
0.16
0.20
[S(+)]

of inversion sensitized with 0.03 M naphthalene in degassed acetonitrile was measured as a function of sulfoxide concentration. The data for (+)-(R)-methyl p-tolyl sulfoxide, 1a, and (+)-(R)-methyl p-chlorophenyl sulfoxide, 1c, are shown in Figure 4. Included in Table I are the data from the inversion and fluorescence quenching experiments for the compounds studied. The correlation between the rate constants determined in these two independent experiments is reasonably good. The error limits quoted are average deviations of a number of runs and the actual deviations may be somewhat larger. The data observed for the five optically active sulfoxides strongly support the proposed mechanism.

The observation (42) that it was not possible to sensitize the inversion of dialkyl sulfoxides with naphthalene is consistent with fluorescence quenching measurements. The intensity of fluorescence of 0.03 M naphthalene in degassed acetonitrile was measured as a function of dimethyl sulfoxide concentration. The rate constant for quenching was found to be $k_Q = (7.5 \pm 0.3)10^5$ M^{-1} sec^{-1}. The quenching rate is at least 20 times slower than that of aryl alkyl sulfoxides, and under normal irradiation conditions a corresponding rate of inversion would be too small to detect.

Figure 4. Quantum yield of sulfoxide inversion sensitized by naphthalene: ● (+)-(R)-methyl p-tolyl sulfoxide, 1a, ▲ (+)-(R)-methyl p-chlorophenyl sulfoxide, 1c.

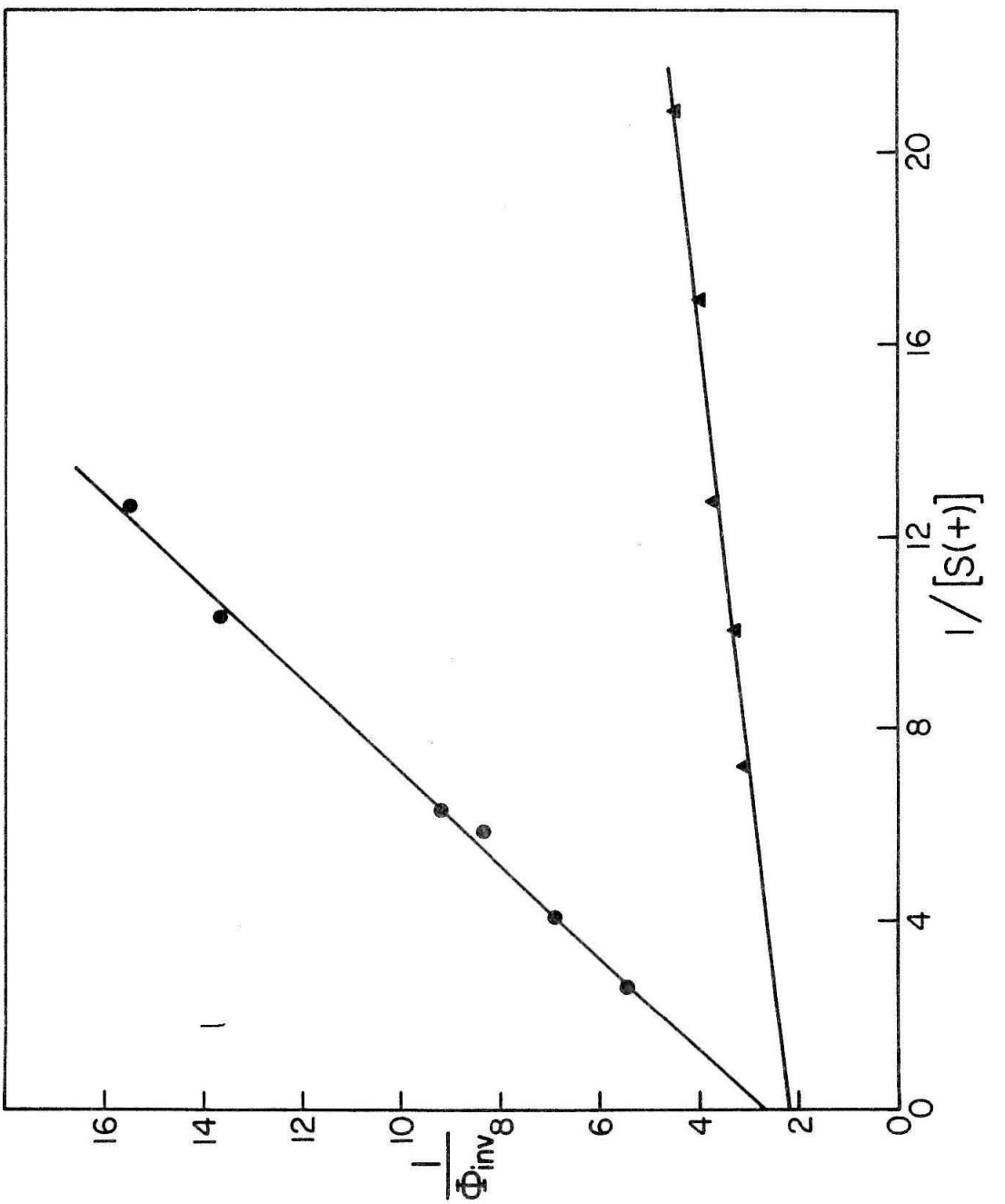
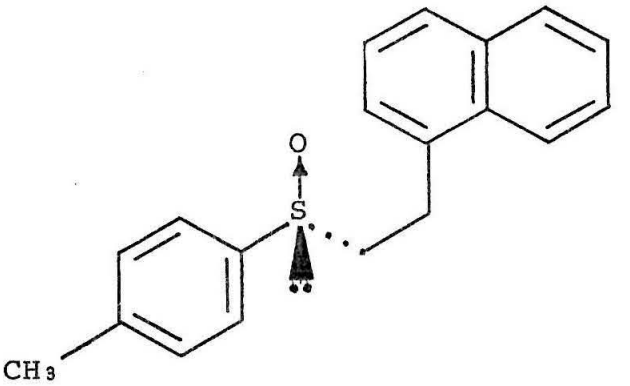

1
$\frac{1}{\Phi_{inv}}$
16
14
12
10
8
6
4
2
0
0
4
8
12
16
20
1/[S(+)]

Table I. Rate Constants for Various Sulfoxides

Sulfoxide	Fluorescence k_Q (M^{-1} sec^{-1})	Inversion k_Q (M^{-1} sec^{-1})
methyl p-tolyl	$(3.2 \pm 0.2)10^7$	$(3.4 \pm 0.3)10^7$
methyl phenyl	$(4.8 \pm 0.5)10^7$	$(5.8 \pm 0.9)10^7$
methyl p-tert-butylphenyl	$(3.4 \pm 0.2)10^7$	$(4.6 \pm 0.3)10^7$
methyl p-bromophenyl	$(7.3 \pm 1.0)10^8$	$(1.3 \pm 0.3)10^9$
methyl p-chlorophenyl	$(2.0 \pm 0.4)10^8$	$(2.7 \pm 0.2)10^8$
methyl p-hydroxyphenyl	$(5.0 \pm 0.2)10^7$	--
chloromethyl p-tolyl	$(2.8 \pm 0.1)10^7$	--

Absorption and Emission Characteristics of (+)-(R)-p-Tolyl 2-(1-naphthyl)ethyl Sulfoxide

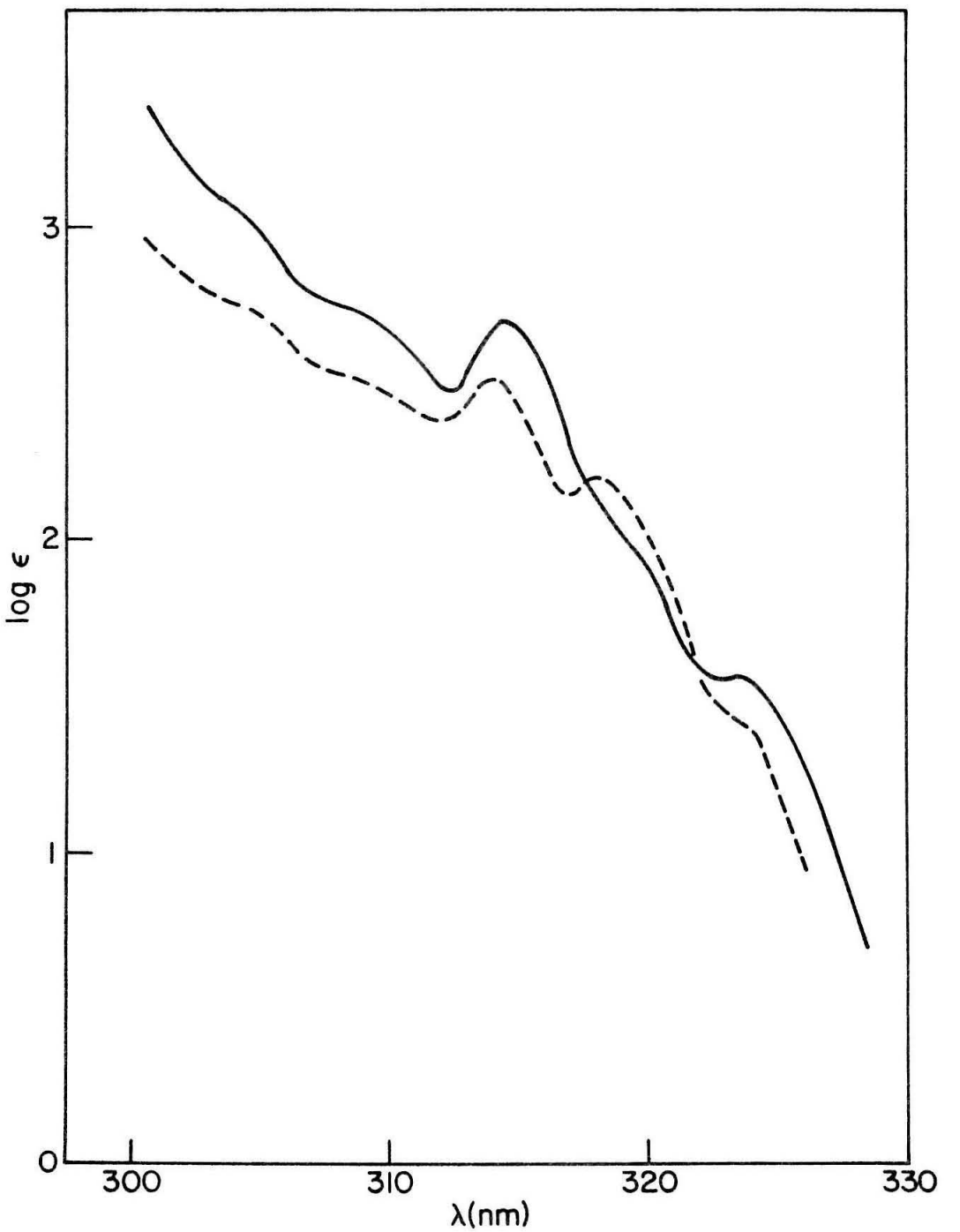
The intramolecular sensitization of stereomutation was also studied in (+)-(R)-p-tolyl 2-(1-naphthyl)ethyl sulfoxide, 2. The absorption spectrum of this compound



2

is compared with that of 1-ethylnaphthalene in Figure 5. Unlike the situation with mixtures of sulfoxide and naphthalene, 2 shows some perturbation of the lowest excited singlet state of naphthalene. The profile is similar to a 1-alkylnaphthalene with differences only in the extinction coefficients so that it is reasonable to assume that excitation is localized in the naphthalene chromophore immediately after absorption. The fluorescence spectrum of 2 is almost identical to that of

Figure 5. Absorption spectra of (+)-(R)-p-tolyl 2-(1-naphthyl)ethyl sulfoxide, 2, ———— and 1-ethylnaphthalene ---------.


log ε
3
2
1
0
300
310
320
330
λ(nm)

1-ethylnaphthalene in position and fine structure. Comparison of the fluorescence intensities of solutions of 0.040 M naphthalene in degassed cyclohexane and 0.0068 M 2 in degassed cyclohexane (matched absorbance at the excitation wavelength of 320 nm) was made. If the quantum yield for fluorescence of naphthalene is taken as $\Phi = 0.29$, then for (+)-(R)-p-tolyl 2-(1-naphthyl)ethyl sulfoxide $\Phi = 0.06$.

It was expected that the intramolecular sensitization of racemization should occur by a mechanism analogous to the one proposed in the intermolecular systems. Such a scheme is shown in the following equations.

$$\text{N-S(+)} \xrightarrow{h\nu} \text{N}^1\text{-S(+)} \qquad (9)$$

$$\text{N}^1\text{-S(+)} \xrightarrow{k_f} \text{N-S(+)} + h\nu' \qquad (10)$$

$$\text{N}^1\text{-S(+)} \xrightarrow{k_o} \text{N-S(+) or N}^3\text{-S(+)} \qquad (11)$$

$$\text{N}^1\text{-S(+)} \underset{k_{-q}}{\overset{k_q}{\rightleftharpoons}} [\text{N-S(+)}]^1 \qquad (12)$$

$$[\text{N-S(+)}]^1 \xrightarrow{k(+)} \text{N-S(+)} \qquad (13)$$

$$[\text{N-S(+)}]^1 \xrightarrow{k(-)} \text{N-S(-)} \qquad (14)$$

$$\text{N}^1\text{-S(+)} + \text{Q} \xrightarrow{k_q} \text{N-S(+)} + \text{Q} \qquad (15)$$

Steps 9-11 represent the normal photophysical processes of 2 when the excitation energy is localized in the naphthalene chromophore. Step 12 shows the reversible formation of a complex in which excitation is spread over the entire molecule, and steps 13 and 14 show the radiationless decay of this exciplex. In order to test this mechanism it is necessary to include an external quencher. The deactivation of the singlet state of 2 by piperylene is shown in step 15.

Kinetic analysis of this mechanism gives the following expressions.

$$\frac{\Phi_{inv_o}}{\Phi_{inv}} = \frac{\Phi_{f_o}}{\Phi_f} = 1 + \tau_s \, k_Q \, [Q]$$

In these equations Φ_{inv_o} = quantum yield of inversion of 2, Φ_{inv} = quantum yield of inversion of 2 with added quencher, and τ_s = singlet lifetime of 2, 9.5 ± 1.0 nsec as determined by the Berlman method (50) under experimental conditions.

Experiments were performed in which the fluorescence of 0.006 M 2 in degassed cyclohexane was measured as a function of added cis-piperylene. A value of k_Q = $(7.2 \pm 0.6)10^7$ $M^{-1}sec^{-1}$ was obtained. The quantum yield of inversion of a 0.006 M solution of 2 in degassed cyclohexane was measured as a function of added cis-piperylene and a value of k_Q = $(7.7 \pm 1.0)10^7$ M^{-1} sec^{-1} was obtained.

The value of Φ_{inv_o} was found to be 0.451 ± 0.004, indicating that the quenching and inversion processes are extremely efficient for this molecule. The agreement between the values of k_Q obtained in these independent experiments is very good. Further indication that the proposed mechanism is valid is provided by comparison of the rate constants with those determined by Stephenson (51) in the intermolecular quenching of substituted naphthalenes with dienes. He found that the rate constant for quenching of 1-methylnaphthalene with trans-piperylene is $k_Q = 7.9 \times 10^7\ M^{-1}\ sec^{-1}$.

Discussion of Exciplex Formation and Decay

It should be pointed out that there is no direct evidence for the postulated exciplex. However, invoking such a species in the mechanism provides a useful framework in which to consider the observed phenomena. The discussion of the individual steps which produce or destroy the exciplex must be largely speculative, but it may provide a basis for further experimental work. The discussion which follows pertains both to the intra- and intermolecular processes.

Of greatest importance is the justification of a step in the mechanism which involves the formation of an excited complex or exciplex. Identical kinetics would be observed if there were a single excited state

which found an unusually rapid mechanism for radiationless decay by dumping vibrational energy in the inversion vibration of the sulfinyl group. This description differs from the one favored (vide infra) both in the lifetime of the encounter of the aromatic hydrocarbon and substrate and in the delocalization of energy originally localized in the sensitizer. This simplest description is passed by because it is difficult to conceive of efficient coupling to high vibrational levels of the sulfinyl group unless some of the electronic excitation is transferred to the group before internal conversion (52).

Also of importance is whether or not the formation of the exciplex is a reversible process. If the formation is an irreversible process, then the composite rate constant, k_Q, in the mechanism suggested is actually the rate constant for the complex formation step. From the experimental results this rate constant is from two to three orders of magnitude below the theoretical diffusion controlled rate in acetonitrile (1.9×10^{10} M^{-1} sec^{-1} at 25°). Intuitively it seems that this is too slow to be reasonable for the rate of establishment of the kind of weak exciton or charge transfer coupling that may be involved between the chromophoric units. Since the quenching rates are well below diffusion controlled, it is inferred that reactions 7 and 8 are rate-limiting and that $k_{-q} >> [k(+) + k(-)]$. These assumptions simplify

the expression for k_Q indicating that quenching reactivity is controlled both by the stability of the complex, measured by k_q/k_{-q}, and by the radiationless decay rate, measured by $[k(+) + k(-)]$.

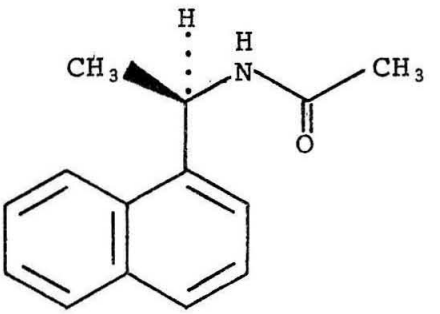
Partial correlation with steric interaction has been observed in the quenching of naphthalene derivatives by conjugated dienes (51). Very recently Solomon, Steel and Weller (53) have obtained reasonable agreement with a partial charge transfer mechanism in the quenching of fluorescence of naphthalene derivatives with quadricyclene. It was the original aim of this study to probe the nature of the naphthalene-sulfoxide exciplex by the use of suitable substituents on the aromatic ring of the substrate. It was felt that the electronic or steric differences in these groups would lead to significant changes in the rate constants for fluorescence quenching and racemization and that these effects would show a clear trend interpretable in terms of some general interaction mechanism. Possibly because of an inability to separate the controlling factors of exciplex stability and rate of radiationless decay, this aim has not been realized. Nevertheless, certain small but real effects should be pointed out although there is no detailed explanation for them.

Fragmentary evidence indicates that a small solvent effect exists on the overall rate of fluorescence

quenching. For solubility reasons, most of the experimental work on the intermolecular quenching mechanism was performed in acetonitrile. For the quenching of naphthalene fluorescence in this solvent by methyl p-tolyl sulfoxide, 1a, the rate constant is $k_Q = (3.2 \pm 0.2)10^7$ M^{-1} sec^{-1}. In cyclohexane this same rate constant is $k_Q = (9.8 \pm 0.9)10^7$ M^{-1} sec^{-1}. Although k_q, which occurs in the numerator of the complex rate constant, k_Q, is expected to be nearly diffusion controlled, the values of k_Q do not vary as the theoretical diffusion rates in the two solvents (6.3×10^9 M^{-1} sec^{-1} for cyclohexane at 17° and 1.7×10^{10} M^{-1} sec^{-1} for acetonitrile at 15°). In fact a good inverse correlation exists although this is probably fortuitous. According to the charge transfer mechanism of Solomon, Steel and Weller (53), the rate constant for fluorescence quenching should be larger in acetonitrile than in cyclohexane because of the large differences in the dielectric constants of the two solvents (38.8 for acetonitrile at 20° and 2.02 for cyclohexane at 20°). However, the rate of radiationless decay of the exciplex is expected to vary inversely with the average energy of interaction with the environment of the molecular vibrational modes of the exciplex and the ground state components (52). This interaction is undoubtedly larger in acetonitrile than in cyclohexane since solvation of the polar sulfoxide group is involved.

If the formation of the exciplex requires a specific geometry of close interaction between the sulfoxide and excited naphthalene molecules, steric effects on the rate constants should be obvious. This is apparently not the case. The rate constant for quenching of naphthalene fluorescence by methyl p-tolyl sulfoxide, 1a, is k_Q = (3.2 ± 0.2)10^7 M^{-1} sec^{-1} while for methyl p-tert-butylphenyl sulfoxide, 1f, it is k_Q = (3.4 ± 0.2)10^7 M^{-1} sec^{-1}. Likewise, the replacement of the methyl group with a chloromethyl group in chloromethyl p-tolyl sulfoxide does not noticeably change the observed fluorescence quenching rate constant, k_Q = (2.8 ± 0.1)10^7 M^{-1} sec^{-1}.

Attempts to observe a diastereomeric rate effect leading to asymmetric induction were unsuccessful. Degassed acetonitrile solutions of 0.011 M (+)-N-acetyl-1-(1-naphthyl)ethyl amine, 3, and 0.094 M (±)-methyl p-bromophenyl sulfoxide, 1b, were irradiated with a 313 nm source with an extimated output of 8 x 10^{-6} einsteins min^{-1} for 48 hours. Isolation and purification of the substrate gave a sample of methyl p-bromophenyl sulfoxide, 1b, with an optical purity of 0.0 ± 0.1%. Apparently any difference in k_Q for the (+)-sulfoxide--(+)-naphthalene or (-)-sulfoxide--(+)-naphthalene pairs is too small to detect. Effects on the value of k_q/k_{-q} may nearly compensate for inverse effects on the value of [k(+) + k(-)].



3

A final observation may be made in the case of halogen substitution of the aromatic ring of the substrate. For methyl p-chlorophenyl sulfoxide, 1c, a value of k_Q = $(2.0 \pm 0.4)10^8$ M^{-1} sec^{-1} is observed, and for methyl p-bromophenyl sulfoxide, 1b, the corrected fluorescence quenching rate constant (vide infra), k_Q, is about 2.7×10^8 M^{-1} sec^{-1}. These values are from four to ten times greater than those observed with any of the other substituents, which vary by less than a factor of two. An electronic effect seems to be ruled out since strongly electron donating substituents, such as R = OH, do not decrease the value of k_Q significantly from that observed when R = H. However, the effect of the halogen

substituent seems to be transmitted through the aromatic ring since methyl p-tolyl sulfoxide, 1a, and chloromethyl p-tolyl sulfoxide have almost identical quenching rate constants. The effect of halogen substituents cannot be one of steric bulk as has been demonstrated above.

The discussion of the key steps of the proposed mechanism have largely concerned the reversible formation of the exciplex. It is of value to consider more carefully the radiationless decay of this species which leads to the observed racemization. Although in steps 7 and 8 of the mechanism a direct conversion of exciplex to ground state molecules is indicated, this is an obvious oversimplification. A more explicit representation of these steps is given by equations 16-19.

$$[N \cdot S(+)]^1 \xrightarrow{[k(+) + k(-)]} N^{*(n)} + S(+)^{*(\nu)} \qquad (16)$$

$$N^{*(n)} \xrightarrow{k_3} N \qquad (17)$$

$$S(+)^{*(\nu)} \xrightarrow{k(+)} S(+) \qquad (18)$$

$$S(+)^{*(\nu)} \xrightarrow{k(-)} S(-) \qquad (19)$$

$N^{*(n)}$ and $S(+)^{*(\nu)}$ represent vibrationally excited electronic ground states of naphthalene and sulfoxide respectively.

The internal conversion reaction must depend in a critical way on coupling of the vibrational modes of both

the sensitizer and the substrate with the electronic excitation of the complex. Theory (52) predicts that internal conversion of the exciplex should be accelerated when the vibrational levels of the individual components in the non-bound electronic ground state of the complex are anharmonic. This is generally the case when one of the constituents may undergo a facile rearrangement upon thermal activation. In this decay some of the 90 kcal $mole^{-1}$ electronic excitation energy appears in the sulfoxide molecule in the form of vibrational energy. The partitioning is such that at least 38.4 kcal $mole^{-1}$, the activation energy for the thermal pyramidal inversion process (36), is localized in the sulfinyl group. This is shown by the values obtained for [k(+) + k(-)]/k(-) given in Table II.

Table II. Partitioning Factors for Various Sulfoxides

Sulfoxide	[k(+) + k(-)]/k(-)
methyl p-tolyl	2.7 ± 0.2
methyl phenyl	2.3 ± 0.3
methyl p-tert-butylphenyl	2.5 ± 0.2
methyl p-chlorophenyl	2.2 ± 0.1
methyl p-bromophenyl	6.5 ± 0.3

Neglecting for the moment the data from (+)-(R)-methyl p-bromophenyl sulfoxide, 1b, one notes that the exciplex decays to give sulfoxide with inverted stereochemistry 37-45% of the time. The value of [k(+) + k(-)]/k(-) is expected to be a number greater than two, that is, complete racemization does not occur, since vibrational deactivation of the sulfoxide will very likely be sufficiently rapid to compete with loss of the original chirality of the substrate. There is no obvious mechanism leading to net reversal of chirality.

The value of [k(+) + k(-)]/k(-) = 6.5 for (+)-(R)-methyl p-bromophenyl sulfoxide, 1b, indicates an interesting change of mechanism which was not totally unexpected. Wilkinson (54) has pointed out that molecules such as bromobenzene are able to catalyze the conversion of the excited singlet states of aromatic hydrocarbons to their triplet states. In the mechanism for (+)-(R)-methyl p-bromophenyl sulfoxide, 1b, it is necessary to include a step represented by the following equation.

$$N^1 + S(+) \xrightarrow{k_c} N^3 + S(+) \qquad (20)$$

Since the singlet-triplet splitting for naphthalene is only 30 kcal $mole^{-1}$, the vibrational energy produced in intersystem crossing is 8 kcal $mole^{-1}$ less than would be required to cross the barrier to inversion of the sulfoxide. Analysis of the mechanism including step 20

indicates that the value of $1/\Phi_{inv}$ at infinite sulfoxide concentration is equal to $(1 + k_c/k_Q)[k(+) + k(-)]/k(-)$. Assuming a normal partitioning factor for the vibrationally excited sulfoxide, it is found that k_c/k_Q is about 1.7. From the observed fluorescence quenching rate constant of 7.3×10^8 M^{-1} sec^{-1}, the values of k_Q = 2.7×10^8 M^{-1} sec^{-1} and $k_c = 4.6 \times 10^8$ M^{-1} sec^{-1} are obtained. The rate constant for quenching of naphthalene fluorescence by bromobenzene determined under identical conditions is $k_c = (3.1 \pm 0.1)10^8$ M^{-1} sec^{-1}. This value is in excellent agreement with the calculated value of k_c.

SUMMARY AND CONCLUSIONS

The naphthalene sensitized photoracemization of some alkyl aryl sulfoxides has been studied. The stereomutation is surprisingly efficient with only a small amount of side reaction occurring. Sensitization by triplet energy transfer has been ruled out on the basis of both spectroscopic and chemical studies. The positions of the singlet states of naphthalene and the sulfoxides preclude exothermic electronic energy transfer. It is postulated that an excited complex, or exciplex, is reversibly formed from an excited singlet state naphthalene molecule and a ground state molecule of the sulfoxide. This species does not have a bound ground state. Deactivation of the exciplex occurs by radiationless decay with conversion of electronic energy to vibrational energy partitioned between the two components. The excited complex does not decay by light emission. In the radiationless process enough vibrational energy appears in the aryl sulfinyl group to effect thermal pyramidal inversion. Support for this mechanism is provided by good correlation between the rates of inversion of the sulfoxide and of quenching of the naphthalene fluorescence.

Kinetic analysis of the proposed mechanism indicates that the rates of inversion or of fluorescence quenching are a function of both the stability of the exciplex and

the rate of radiationless decay. By varying the substitution of the aromatic ring of the sulfoxide, a rate correlation with steric and electronic effects was sought. Possibly because of an inability to separate the two factors controlling the rates, this aim has not been realized although some minor effects have been observed.

"In many cases preliminary understanding of the mechanisms of photoreactions are more easily derived from study of sensitized reactions than from study of those involving direct excitation" (42). This has not been true in the research into the photoracemization of sulfoxides. Instead, the studies have led to the elucidation of an example of a newly recognized type of energy transfer. Naive theories about excited complex formation and radiationless decay have developed somewhat in the course of this investigation. However, it is also apparent that some studies which appeared promising have been remarkably unsuccessful. It is not difficult to learn from these failures and to design better experiments in light of a slightly modified theory. Indeed, this is the course that most of the research on the production and destruction of exciplexes has taken. Unfortunately a point of diminishing returns seems to have been reached in the case of the photoracemization of sulfoxides. A better approach may be to return to the basic problem

which led to this research. A detailed study of the racemization of sulfoxides upon direct irradiation may provide insight into one or more of the steps in the complicated mechanism of exciplex formation and decay.

EXPERIMENTAL

Materials

Sensitizers

Naphthalene (Eastman) was recrystallized twice from ethanol and sublimed at 50°/0.05 mm. The material had a melting point of 79.5-80.0°. Benzophenone (Eastman) was recrystallized twice from 60/70 petroleum ether and sublimed at 40°/0.05 mm. The material had a melting point of 49.0-49.5°. Purification of 1-ethylnaphthalene (J.T. Baker) was by distillation at 135-136°/20 mm. (+)-N-acetyl-1-(1-naphthyl) ethyl amine, 3, was prepared by a modification of the procedure of Cole (55). A solution of 4.094 grams of (+)-1-(1-naphthyl) ethyl amine (K & K Laboratories) (0.0239 mole) and 9.0 ml of acetic acid was placed in a 100-ml round-bottomed flask and heated to 100°. The mixture was removed from the oil bath and to it were added 6.5 grams of acetic anhydride (0.063 mole). The reaction mixture was allowed to stand for one minute and was quenched by the addition of 25 grams of ice. The solvents were removed by flash evaporation and the amide was recrystallized twice from toluene to give 3.853 grams of (+)-N-acetyl-1-(1-naphthyl) ethyl amine, 3, (76%). The compound had a melting point of 157.0-158.5° (lit. mp: 155°)(55). The specific rotation was $[\alpha]_D^{25}$=+123° (c 2.4, chloroform) (lit. $[\alpha]_D^{25}$=+120° (c 2.5,

chloroform)) (55). The infrared spectrum ($CHCl_3$) had strong bands at 1670 and 1514 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ1.53 (3H,d J=6.5 Hz), 1.81 (3H,s), 5.88 (1H,q J=6.5 Hz), 6.44 (1H,m), and 7.2-8.2 (7H,m).

Solvents

Acetonitrile (Matheson, Coleman and Bell) was distilled three times from phosphorous pentoxide and once from anhydrous potassium carbonate. Then it was distilled with no drying agent through a 60-cm column packed with glass helices. Only the middle fraction boiling at 80.0° was taken. Cyclohexane (Matheson, Coleman and Bell) was stirred at reflux with sulfuric acid under a nitrogen blanket for three days. The sulfuric acid was changed every 24 hours. Then it was washed with sodium bicarbonate solution and water, dried over magnesium sulfate, filtered and distilled from phosphorous pentoxide through a 60-cm column packed with glass helices. Only the middle fraction boiling at 81.0° was taken. Normal hexane (Phillips) was purified by the method used for cyclohexane. It was distilled from sodium through a 60-cm column packed with glass helices. Only the middle fraction boiling at 68.0° was taken. Diethyl ether (Mallinckrodt) for phosphorescence measurements was distilled at 35.0° from lithium aluminum hydride under a nitrogen blanket just prior to use. Ethanol (U.S. Industrial

Chemicals) for phosphorescence measurements was refluxed over magnesium turnings and distilled at 78.5° just prior to use.

Sulfoxides

Infrared spectra were obtained on a Perkin Elmer 257 Grating Infrared Spectrometer or a Beckman IR 7 Infrared Spectrometer. NMR spectra were measured on a Varian A-60A Spectrometer. Ultraviolet spectra were measured on a Cary 14 Recording Spectrophotometer. The polarimetric measurements were made on a Winkel-Zeiss Polarimeter or a Perkin Elmer 141 Polarimeter. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

(±)-Methyl p-tolyl sulfoxide, 1a, was prepared by a procedure analogous to that of Leonard (56). A solution of 40.60 grams of sodium metaperiodate (0.190 mole) in 200 ml of water and 200 ml of methanol was added to a three-necked flask equipped with an overhead stirrer and cooled in an ice--water bath. In one portion 24.97 grams of methyl p-tolyl sulfide (Eastman) (0.181 mole) were added. The mixture was stirred at 0° for 16 hours. The sodium iodate was filtered, and the filter cake was washed with methanol. The filtrate was extracted several times with chloroform, and the extracts were dried over magnesium sulfate, filtered and flash evaporated. The residual oil was treated with 30/60 petroleum ether and

cooled. The yield of crystalline material was 24.59 grams (88%). Final purification was effected by sublimation at 42°/0.05 mm. The compound had a melting point of 45.5-48.0° (lit. mp: 42-43°) (57). The infrared spectrum ($CHCl_3$) showed a strong band at 1036 cm^{-1}. The nmr spectrum ($CHCl_3$--1% TMS) had signals at δ 2.40 (3H, s), 2.68 (3H, s) and 7.49 (4H, A_2B_2). The ultraviolet spectrum had (C_2H_5OH) λ_{max} 237.0 nm (6230) and λ_{sh} 217.5 nm (8750); (C_6H_{12}) λ_{max} 250.0 nm (4870) and λ_{sh} 217.5 nm (9770); (CH_3CN) λ_{max} 243.0 nm (5190) and λ_{sh} 217.5 nm (9000).

A similar periodate oxidation method and work-up was employed in the preparation of (±)-methyl p-bromophenyl sulfoxide, 1b, (±)-methyl p-chlorophenyl sulfoxide, 1c, (±)-methyl phenyl sulfoxide, 1e, and (±)-methyl p-tert-butylphenyl sulfoxide, 1f.

(±)-Methyl p-bromophenyl sulfoxide, 1b, was prepared in 91% yield by the sodium metaperiodate oxidation (56) of p-bromoanisole (Aldrich) at 0° over 16 hours. Final purification was effected by recrystallization from 5% chloroform--95% toluene and sublimation at 75°/0.05 mm. The compound had a melting point of 82.5-84.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1050 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 2.70 (3H, s) and 7.58 (4H, A_2B_2). The ultraviolet spectrum (CH_3CN) had λ_{max} 250.0 nm (6750) and 222.0 nm (11300).

Anal. Calcd for C_7H_7BrOS: C, 38.37; H, 3.22;

S, 14.63; Br, 36.47. Found: C, 38.38; H, 3.17; S, 14.62; Br, 36.50.

(±)-Methyl p-chlorophenyl sulfoxide, 1c, was prepared in 80% yield by the sodium metaperiodate oxidation (56) of p-chloroanisole (Wateree Chemical Co.) at 0° for 24 hours. Purification was effected by chromotography on silica gel , recrystallization from toluene and sublimation at 50°/0.035 mm. The compound had a melting point of 46.0-48.2° (lit. mp: 47-48°)(57). The infrared spectrum ($CHCl_3$) showed a strong band at 1050 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 2.72 (3H, s), and 7.57 (4H, A_2B_2). The ultraviolet spectrum (CH_3CN) had λ_{max} 248.5 nm (5650) and 220.0 nm (11200).

Anal. Calcd for C_7H_7ClOS: C, 48.14; H, 4.04; Cl, 20.30; S, 18.36. Found: C, 48.30; H, 3.99; Cl, 20.39; S, 18.41.

(±)-Methyl phenyl sulfoxide, 1e, was prepared in 79% yield by the sodium metaperiodate oxidation (56) of methyl phenyl sulfide (Calbiochem) at 4° for 48 hours. Final purification was effected by Kugelrohr distillation at 95°/0.2 mm (lit. bp: 83-85°/0.1 mm)(56). The infrared spectrum ($CHCl_3$) showed a strong band at 1040 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 2.68 (3H, s) and 7.3-7.8 (5H, m).

(±)-Methyl p-tert-butylphenyl sulfoxide, 1f. To a solution of 16.6 grams of p-tert-butylbenzene thiol (Matheson, Coleman and Bell) (0.10 mole), 30 ml of water and

4.0 grams of sodium hydroxide (0.10 mole) were added with stirring 14.2 grams of methyl iodide (0.10 mole) over the course of 30 minutes. The two-phase system was stirred an additional hour making sure that the aqueous layer remained basic. The reaction mixture was extracted with ether, and the extracts washed with brine, dried over magnesium sulfate, filtered and flash evaporated to give 16.8 grams of methyl p-tert-butylphenyl sulfide (94%). The compound had a boiling point of 50.0-56.0°/0.10 mm. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 2.37 (3H, s), 1.27 (9H, s) and 7.23 (4H, A_2B_2). (±)-Methyl p-tert-butylphenyl sulfoxide, 1f, was prepared in 65% yield by the sodium metaperiodate oxidation (56) of the sulfide at 0° for 19 hours. The product was purified by column chromatography on silica gel, recrystallization from 5% toluene--95% hexane and sublimation at 70°/0.05 mm. The compound had a melting point of 76.0-77.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1047 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 2.71 (3H, s), 1.34 (9H, s) and 7.60 (4H, s). The ultraviolet spectrum (CH_3CN) had λ_{max} 244.0 nm (5890) and λ_{sh} 217.5 nm (10100).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.36; H, 8.28; S, 16.38.

(±)-Methyl p-hydroxyphenyl sulfoxide, 1e, was

prepared by a modification of the procedure of Bordwell (58). A solution of 12.1 grams of 4-(methylthio)phenol (Crown Zellerbach) (0.087 mole), 194 grams of pyridine and 750 ml of benzene was placed in a 2000-ml round-bottom flask equipped with a magnetic stirrer. To this solution were added 19.0 grams of benzoyl chloride (0.135 mole). The solution was stirred at room temperature for 12 hours. The mixture was stirred for an additional 2 hours after the addition of 400 ml of water. The reaction mixture was extracted with chloroform, and the extracts were washed with 10% hydrochloric acid followed by 10% potassium carbonate solution, dried over magnesium sulfate, filtered and flash evaporated. The yield of 4-(methylthio)phenyl benzoate was 18.5 grams (88%). The compound had a melting point of 110-112°. A solution of 26.2 grams of the benzoate (0.107 mole) in 500 ml of acetone and 500 ml of acetic acid was placed in a 2000-ml three-necked flask equipped with a magnetic stirrer and an addition funnel. The mixture was cooled to 0° and 13.4 grams of 30% hydrogen peroxide (0.118 mole) were added dropwise with stirring. The solution was allowed to come to room temperature over the course of about 10 hours. The reaction mixture was flash evaporated, and the crude yellow crystals were recrystallized from toluene to give 25.9 grams of (±)-methyl p-benzyloxyphenyl sulfoxide (93%). The compound had a melting point of 152.5-154.0°.

The infrared spectrum ($CHCl_3$) had strong bands at 1740 and 1060 cm^{-1}. A solution of 0.502 grams of the sulfoxide (0.0019 mole) in 25 ml of 10% aqueous sodium hydroxide was stirred for 48 hours at 30°. The solution was saturated with carbon dioxide and extracted with ether using a continuous liquid-liquid extractor. The extracts were dried over magnesium sulfate, filtered and flash evaporated. The crude product was recrystallized from 5% chloroform--95% toluene and sublimed at 100°/0.05 mm to give 0.173 grams (57%) of (±)-methyl p-hydroxyphenyl sulfoxide, 1e. The compound had a melting point of 103.5-105.0° (lit. mp: 103.5-104.0°) (58). The infrared spectrum ($CHCl_3$) showed a strong band at 1040 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 2.75 (3H, s), 7.28 (4H, A_2B_2) and 9.17 (1H, s). The ultraviolet spectrum (CH_3CN) showed λ_{sh} 280.0 nm (1500), λ_{max} 242.0 nm (8950) and 230.0 nm (8600).

(±)-Chloromethyl p-tolyl sulfoxide. A solution of 8.58 grams of thionyl chloride (0.072 mole) in 20 ml of methylene chloride was placed in a three-necked flask equipped with a magnetic stirrer, reflux condensor and an addition funnel. The solution was heated to reflux and a solution of 9.27 grams of (±)-methyl p-tolyl sulfoxide, 1a, (0.060 mole) in 30 ml of methylene chloride was added over the course of one hour. The reaction mixture was heated under reflux for an additional two hours.

The solvent was flash evaporated, and the residual oil was distilled under vacuum to give 9.27 grams of pale yellow chloromethyl p-tolyl sulfide (89%). The compound had a boiling point of 54.0-57.0°/0.05 mm. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 2.27 (3H, s), 4.82 (2H,s) and 7.25 (4H, A_2B_2). Attempted oxidation of this sulfide using sodium metaperiodate led to extensive decomposition. A solution of 3.00 grams of chloromethyl p-tolyl sulfide (0.0174 mole) in 80 ml of chloroform was added to a round-bottomed flask equipped with a magnetic stirrer. The solution was cooled to -5°, and 3.88 grams of 85% m-chloroperbenzoic acid (0.0191 mole) were added at a rate such that the temperature of the reaction mixture did not exceed 0°. The mixture was stirred at room temperature overnight, washed with saturated sodium bicarbonate solution followed by water, dried over magnesium sulfate, filtered and flash evaporated. The residual oil was chromatographed on silica gel, recrystallized from 50% hexane--50% xylene and sublimed at 50°/0.035 mm to give 2.928 grams of (±)-chloromethyl p-tolyl sulfoxide (89%). The compound had a melting point of 59.8-61.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1056 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 2.40 (3H, s), 4.40 (2H, AA'), 7.48 (4H, A_2B_2). The ultraviolet spectrum (CH_3CN) showed λ_{max} 247.5 nm (6000) and λ_{sh} 219.0 nm (9800).

Anal. Calcd for C_8H_9ClOS: C, 50.93; H, 4.81; S, 16.99; Cl, 18.79. Found: C, 50.88; H, 4.89; S, 17.01; Cl, 18.81.

(+)-(R)-Methyl p-tert-butylphenyl sulfoxide, 1f. Conversion of tert-butylbenzene (Matheson, Coleman and Bell) to p-tert-butyl-nitrobenzene was effected in 56% yield using the nitration procedure of Brown (59) followed by separation of isomers by spinning band distillation at 10 mm. The isomeric purity was shown to be greater than 99% by vpc analysis. The compound had a boiling point of 78-83°/0.08-0.06 mm. The infrared spectrum (liquid film) showed strong bands at 1525 and 1350 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 1.35 (9H, s) and 7.83 (4H, A_2B_2). A mixture of 147.5 grams of p-tert-butyl-nitrobenzene (0.825 mole) and 75 ml of ethanol was placed in a 500-ml Parr Shaker bottle with 1.50 grams of 85% platinum oxide. Hydrogenation was carried out over the course of 8 hours at pressures of 3.4-1.0 atmospheres of hydrogen. The reaction mixture was filtered through Cellite and flash evaporated. Distillation of the residual oil gave 113.4 grams of p-tert-butylaniline (92%). The compound had a boiling point of 55.0-56.0°/0.04-0.03 mm. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 1.23 (9H, s), 3.38 (2H, s) and 6.80 (4H, A_2B_2).

Conversion of the aromatic amine to a sulfinic acid

was effected using a modification of the procedure of Gattermann (60). A similar method and work-up was employed in the preparation of p-bromobenzenesulfinic acid and p-chlorobenzenesulfinic acid. Detailed experimental procedures will not be given for these compounds.

A mixture of 62.4 grams of p-tert-butylaniline (0.418 mole) and 1050 ml of water was placed in a 3000-ml three-necked flask equipped with an overhead stirrer, a thermometer and an addition funnel. Slow addition of 180 grams of sulfuric acid and heating of the reaction mixture to 80° gave a clear solution of the amine salt. The solution was cooled to 2°. A solution of 31.8 grams of sodium nitrite (0.460 mole) in 150 ml of water was added dropwise with stirring until the solution gave a positive starch-iodine test. An ice-cold mixture of 230 grams of sulfuric acid and 115 ml of water was added. Cold, water-saturated sulfur dioxide was bubbled into the stirred solution of diazonium salt until the uptake was 248 grams (15.5 grams/100 ml). About 250 grams of copper paste were added over the course of 2 hours. The bubbling of sulfur dioxide was continued to maintain saturation. The solution was stirred an additional 2 hours at 2°. The reaction mixture was filtered. In a separate filtration, the filter cake was washed first with water and then with 5% ammonium hydroxide solution. The acidic filtrate was extracted twice with ether. The ether

extracts were flash evaporated, and the residual material was taken up in water made acidic to Congo Red. The basic filtrate was acidified with 50% sulfuric acid. Both acidic solutions were treated with excess saturated ferric chloride solution. The orange ferric sulfinate was filtered and washed with water. The salt was slurried in distilled water and made basic with 15% sodium hydroxide. The ferric hydroxide was filtered off, and the filter cake was washed with 5% sodium hydroxide solution. The filtrate was acidified with 50% sulfuric acid and extracted three times with ether. The organic phase was dried over magnesium sulfate, filtered and flash evaporated. The brown oil crystallized on standing and was dried at 25°/0.05 mm for 1 hour. The yield of p-tert-butylbenzenesulfinic acid was 34.3 grams (42%). The compound had a melting range of 59.0-63.0°. The infrared spectrum ($CHCl_3$) showed a strong band at 1082 cm^{-1}.

The sulfinic acid was converted to the corresponding (-)-menthyl-(-)-sulfinate by a sequence similar to that of Herbrandson (61). All of the sulfinic acids were treated in this manner, and detailed experimental procedure will not be given for the other compounds.

In a 500-ml three-necked flask equipped with an overhead stirrer, an addition funnel and a drying tube were placed 19.3 grams of p-tert-butylbenzenesulfinic acid (0.098 mole). To this were added 115 ml of thionyl

chloride with stirring. After addition was complete, the reaction mixture was stirred an additional 2 hours. The solution was flash evaporated, and the final traces of thionyl chloride were azeotroped off with benzene.

The sulfinyl chloride in 200 ml of ether was placed in a 1000-ml three-necked flask equipped with an overhead stirrer, a nitrogen inlet and an addition funnel. The solution was cooled to 0° and flushed with nitrogen. A solution of 15.2 grams of l-menthol (0.098 mole), 15 ml of pyridine (0.185 mole) and 150 ml of ether was added dropwise with stirring. The reaction mixture was stirred an additional 2 hours. A 1% solution of hydrochloric acid was added until two clear phases obtained. The organic phase was washed twice with 1% hydrochloric acid and twice with water. The ether layer was dried over magnesium sulfate, filtered and flash evaporated. The residual oil was dried at 25°/0.05 mm. The (-)-menthyl (±)-p-tert-butylbenzenesulfinate obtained from 53.6 grams of sulfinic acid was taken up in 60/70 petroleum ether and treated with a stream of anhydrous hydrogen chloride for a period of 15 minutes. The solution was slowly cooled to 0° and the crystalline sulfinate was filtered and triturated with 60/70 petroleum ether at -70°. The mother liquors were treated in this same manner three more times. The yield of (-)-menthyl (-)-p-tert-butylbenzenesulfinate was 66.6 grams (73%). Final

purification was effected by careful recrystallization from 60/70 petroleum ether to constant rotation. The compound had a melting point of 99.5-102.5°. The specific rotation was $[\alpha]_D^{25} = -171.9°$ (c 1.9, chloroform). The infrared spectrum (CCl_4) showed a strong band at 1146 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals (inter alia) at δ 4.15 (1H, m), 1.33 (9H, s) and 7.61 (4H, A_2B_2).

The (-)-menthyl (-)-sulfinate was converted to the corresponding (+)-(R)-sulfoxide by a procedure analogous to that of Andersen (19). This method was used for the preparation of all of the optically active sulfoxides. Detailed experimental procedure will only be given for (+)-(R)-methyl p-tert-butylphenyl sulfoxide, 1f.

A solution of 16.476 grams of (-)-menthyl-(-)-p-tert-butylbenzenesulfinate (0.049 mole) in 140 ml of ether was placed in a 1000-ml three-necked flask equipped with an overhead stirrer, a drying tube and an addition funnel. A solution of methyl magnesium iodide (0.065 mole) in 100 ml of ether was added dropwise with stirring. After addition was complete, 150 ml of tetrahydrofuran was added followed by 140 ml of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted several times with chloroform. The combined organic phases were dried over magnesium sulfate, filtered and flash evaporated to give a red oil. The menthol was removed from this mixture by steam

distillation from 200 ml of 20% potassium hydroxide solution over the course of an hour. The residue was cooled and extracted with methylene chloride. The extracts were washed with brine, dried over magnesium sulfate, filtered and flash evaporated. The crude sulfoxide was chromatographed on silica gel and final purification was effected by sublimation at 56°/0.05 mm. The yield of (+)-(R)-methyl p-tert-butylphenyl sulfoxide, 1f, was 6.400 grams (66%). The compound had a melting point of 51.0-54.0°. The specific rotation was $[\alpha]_D^{25} = +107.9°$ (c 2.4, acetone). The infrared spectrum ($CHCl_3$) showed a strong absorption at 1050 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 2.71 (3H, s), 1.35 (9H, s) and 7.62 (4H, s).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.44; H, 8.27; S, 16.25.

(+)-(R)-Methyl p-bromophenyl sulfoxide, 1b. The procedure of Gattermann (60) was used to convert p-bromoaniline (Matheson, Coleman and Bell) to p-bromobenzenesulfinic acid in 68% yield after purification through the ferric salt. The compound had a melting point of 104-110° (lit. mp: 114-115°) (60). The infrared spectrum (nujol) showed a strong band at 1057 cm^{-1}. The acid was converted to p-bromobenzenesulfinyl chloride and then directly to (-)-menthyl (±)-p-bromobenzenesulfinate by a procedure

analogous to that of Herbrandson (61). A solution of the diastereomers in 60/70 petroleum ether was treated with anhydrous hydrogen chloride, flash evaporated and crystallized from acetone. The procedure was repeated several times with the mother liquors until a 61% yield of (-)-menthyl (-)-p-bromobenzenesulfinate was obtained. Final purification was effected by recrystallization from 60/70 petroleum ether to constant rotation. The material had a melting range of 108.0-113.5°. The specific rotation was $[\alpha]_D^{25} = -159.8°$ (c 2.7, chloroform). The infrared spectrum (CCl_4) showed a strong band at 1145 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed (inter alia) signals at δ 4.22 (1H, m) and 7.67 (4H, A_2B_2). Treatment of the sulfinate with methyl magnesium iodide by a procedure analogous to that of Andersen (19) gave (+)-(R)-methyl p-bromophenyl sulfoxide, 1b, in 56% yield. Final purification was effected by column chromatography on silica gel and sublimation at 70°/0.05 mm. The compound had a melting point of 73.5-78.0°. The specific rotation was $[\alpha]_D^{25} = +103.7°$ (c 1.2, acetone). The infrared spectrum (CCl_4) showed a strong doublet at 1061 and 1069 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 2.73 (3H, s) and 7.62 (4H, A_2B_2).

Anal. Calcd for C_7H_7BrOS: C, 38.37; H, 3.22; S, 14.63; Br, 36.47. Found: C, 38.46; H, 3.22; S, 14.69; Br, 36.41.

(+)-(R)-Methyl p-chlorophenyl sulfoxide, 1c. The procedure of Gattermann (60) was used to convert p-chloroaniline (Eastman) to p-chlorobenzenesulfinic acid in 59% yield after purification through the ferric sulfinate salt. The compound had a melting point of 96.0-99.0° (lit. mp: 93-94°) (60). The infrared spectrum (nujol) showed a strong band at 1050 cm^{-1}. The acid was converted first to p-chlorobenzenesulfinyl chloride and then to (-)-menthyl (±)-p-chlorobenzenesulfinate by a sequence analogous to that of Herbrandson (61). By a procedure identical to that used for (-)-menthyl (-)-p-bromobenzenesulfinate a 69% yield of (-)-menthyl (-)-p-chlorobenzenesulfinate was isolated. Final purification was by recrystallization to constant rotation from 60/70 petroleum ether. The material had a melting range of 82.5-86.0°. The specific rotation was $[\alpha]_D^{25}$= -183.6° (c 5.5, chloroform). The infrared spectrum (CCl_4) showed a strong band at 1145 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed (inter alia) signals at δ 4.14 (1H, m) and 7.57 (4H, A_2B_2). The sulfinate was converted to (+)-(R)-methyl p-chlorophenyl sulfoxide, 1c, in 92% yield with methyl magnesium iodide by a method analogous to that of Andersen (19). Final purification was effected by column chromatography on silica gel and sublimation at 45°/0.035 mm. The compound had a melting point of 45.5-48.0°. The specific rotation was

$[\alpha]_D^{25}$= +124.7° (c 7.8, acetone). The infrared spectrum ($CHCl_3$) showed a strong band at 1049 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) showed absorptions at δ 2.72 (3H, s) and 7.58 (4H, A_2B_2).

Anal. Calcd for C_7H_7ClOS: C, 48.14; H, 4.04; S, 18.36; Cl, 20.30. Found: C, 48.23; H, 4.04; S, 18.36; Cl, 20.38.

(+)-(R)-Methyl phenyl sulfoxide, 1e. A solution of 400 grams of sodium sulfite (3.1 mole), 280 grams of sodium bicarbonate (3.3 mole) and 1.6 liters of water was placed in a 3000-ml three-necked flask equipped with an overhead stirrer and an addition funnel. The solution was heated to 75°. To the flask was added 300 grams of benzenesulfonyl chloride (Aldrich)(1.70 mole) over the course of three hours. The solution was stirred at 75° an additional hour under a nitrogen stream to bring the volume back to 1.6 liters. The mixture was cooled to room temperature, and the crystalline salt was filtered. After purification through the ferric sulfinate salt, 138.0 grams of benzenesulfinic acid were obtained (58%). The compound had a melting point of 80.0-82.5°. The infrared spectrum ($CHCl_3$) showed a strong triplet at 1070, 1081 and 1097 cm^{-1}. The acid was converted first to benzenesulfinyl chloride and then to (-)-menthyl (±)-benzenesulfinate by the procedure of Herbrandson (61). The excess l-menthol, which made crystallization

impossible, was distilled off at 60°/0.1 mm. The mixture of diastereomers was taken up in three volumes of methanol and cooled to -78°. The crystalline sulfinate was filtered off, and the filtrate was flash evaporated and then treated with anhydrous hydrogen chloride for 5 minutes. The procedure was repeated three times to give a 25% yield of (-)-menthyl (-)-benzenesulfinate. Final purification was effected by careful recrystallization from methanol to constant rotation. The compound had a melting point of 49.0-50.5° (lit. mp: 49-51°)(61). The specific rotation was $[\alpha]_D^{25}$= -201.8° (c 2.5, acetone) (lit. $[\alpha]_D^{25}$= -205.5° (c 2.0, acetone))(61). The infrared spectrum ($CHCl_3$) showed a strong band at 1135 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals (inter alia) at δ 4.15 (1H, m) and 7.4-7.9 (5H, m). The sulfinate was converted to (+)-(R)-methyl phenyl sulfoxide, 1e, in 65% yield with methyl magnesium iodide by a method analogous to that of Andersen (19). Final purification was effected by column chromatography on silica gel and vacuum distillation. The compound had a boiling range of 70-80°/0.10-0.15 mm. The specific rotation was $[\alpha]_D^{25}$ = +142.4° (c 5.5, acetone)(lit. $[\alpha]_D^{25}$ = +149°)(31). The infrared spectrum (liquid film) showed a strong band at 1063 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 2.70 (3H, s) and 7.4-7.8 (5H,m). The ultraviolet spectrum (CH_3CN) had λ_{max} 244.0 nm (3580).

(+)-(R)-Methyl p-tolyl sulfoxide, 1a. Sodium p-toluenesulfinate dihydrate (Eastman) was first converted to p-toluenesulfinyl chloride and then to (-)-menthyl (±)-p-toluenesulfinate by a sequence analogous to that of Herbrandson (61). The mixture of diastereomers was recrystallized from hexane to constant rotation. The yield of (-)-menthyl (-)-p-toluenesulfinate was 39 %. The compound had a melting point of 103.5-106.5° (lit. mp: 106-107°)(62). The specific rotation was $[\alpha]_D^{25}$= -201° (c 3.4, acetone) (lit. $[\alpha]_D^{25}$= -199.19°) (62). The infrared spectrum ($CHCl_3$) showed a strong doublet at 1114 and 1127 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals (inter alia) at δ 2.38 (3H, s), 4.10 (1H, m) and 7.45 (4H, A_2B_2). The sulfinate was converted to (+)-(R)-methyl p-tolyl sulfoxide, 1a, in 66% yield by treatment with methyl magnesium iodide according to the procedure of Andersen (19). Final purification was effected by chromatography on silica gel and sublimation at 62°/0.05 mm. The compound had a melting point of 74.5-78.5° (lit. mp: 73.0-74.5°) (21). The specific rotation was $[\alpha]_D^{25}$= +144° (c 3.8, acetone) (lit. $[\alpha]_D^{25}$= +145.5° (acetone)) (21). The infrared spectrum ($CHCl_3$) had a strong band at 1036 cm^{-1}. The nmr spectrum ($CDCl_3$--1%TMS) had signals at δ 2.38 (3H, s), 2.67 (3H, s) and 7.44 (4H, A_2B_2).

(+)-(R)-2-(1-naphthyl)ethyl p-tolyl sulfoxide, 2.

A mixture of 15.2 grams of lithium aluminum hydride (1.6 equivalent) and 200 ml of dry ether was placed in a 1000-ml three-necked flask equipped with an overhead stirrer, a good condensor and an addition funnel. A solution of 18.6 grams of 1-naphthylacetic acid (Eastman) (0.3 equivalent) in 300 ml of ether was added dropwise with stirring. After the addition was complete, the reaction mixture was refluxed for an additional hour. To the flask were carefully added with rapid stirring 15.2 ml of water followed by 15.2 ml of 15% sodium hydroxide solution and 45 ml of water. The granular white precipitate was filtered and washed with ether. The ether filtrate was dried over magnesium sulfate, filtered and flash evaporated to give 16.36 grams of 2-(1-naphthyl)ethanol (95%). The compound had a melting point of 60.0-62.0°. The infrared spectrum ($CHCl_3$) showed bands at 3625 and 3465 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 1.84 (1H, s), 3.24 (2H, t J=6.5 Hz), 3.88 (2H, t J=6.5 Hz), and 7.2-8.2 (7H, m). A slurry of 16.09 grams of the alcohol (0.0935 equivalent) in 30 ml of benzene was placed in a three-necked flask equipped with a magnetic stirrer, a reflux condensor and an addition funnel. The mixture was cooled to 0° with stirring. A solution of 12.85 grams of freshly distilled phosphorous tribromide (0.142 equivalent) in 25 ml of benzene was added dropwise to the alcohol. The

solution was stirred an additional hour at 0° and then for 3 hours at 60°. The reaction mixture was poured onto 100 grams of ice. The benzene layer was separated, and the aqueous layer was extracted several times with benzene. The combined benzene extracts were washed with brine, dried over magnesium sulfate, filtered and flash evaporated. The resulting oil was vacuum distilled to give 14.96 grams of 2-(1-naphthyl)ethyl bromide (68%). The compound had a boiling point of 117°/0.04 mm. The nmr spectrum ($CDCl_3$--1% TMS) showed signals at δ 7.2-8.0 (7H, m) and 3.47 (4H, s). A solution of the Grignard reagent, 2-(1-naphthyl)ethyl magnesium bromide (0.062 mole), in 150 ml of ether was prepared and added to (-)-menthyl (-)-p-toluenesulfinate (0.048 mole) following the procedure of Andersen (19). The yield of (+)-(R)-2-(1-naphthyl)ethyl p-tolyl sulfoxide, 2, was 44% after purification by chromatography on silica gel and recrystallization from 5% acetone--95% 60/70 petroleum ether. The compound had a melting point of 71.5-73.0° (lit. mp: 72-73°) (41). The specific rotation was $[\alpha]_D^{25}$= +131° (c 0.56, ethanol) (lit. $[\alpha]_D^{25}$= +132° (ethanol)) (41). The infrared spectrum ($CHCl_3$) showed a strong doublet at 1035 and 1045 cm^{-1}. The nmr spectrum ($CDCl_3$--1% TMS) had signals at δ 2.40 (3H, s), 2.9-3.7 (4H, m) and 7.2-8.0 (11H, m). The ultraviolet spectrum (C_6H_{12}) showed (inter alia) λ_{max} 323.8 nm (37) and

314.4 nm (500).

Physical Measurements

Fluorescence Quenching Studies

Corning 13 mm pyrex tubes were used to hold samples for both fluorescence quenching studies and quantum yield determinations. They were carefully washed with Orvus (Proctor and Gamble) and rinsed repeatedly with distilled water and finally with reagent grade methanol. The tubes were dried in an oven for several hours and then constricted to facilitate sealing.

Solutions for fluorescence quenching experiments were generally prepared in 10-ml volumetric flasks by the addition of a weighed portion of quencher and an aliquot of a stock solution of naphthalene. Aliquots of 3.0 ml were delivered into the preconstricted tubes. The samples were degassed by three freeze-pump-thaw cycles at a final pressure of 5×10^{-4} mm and sealed.

Measurements of the intensity of fluorescence of naphthalene as a function of quencher concentration were performed on an Aminco Bowman Spectrophotofluorimeter. An excitation wavelength of 320 nm was found to maximize the intensity of emission. The sample containing only naphthalene was placed in the instrument and the sensitivity was adjusted to give close to full scale deflection. Without changing any of the instrument settings

the fluorescence spectra of the quenched samples were measured. The series of measurements was repeated without readjustment to guard against major lamp fluctuations. In general the intensity of fluorescence, measured by maximum peak height, was reproducible to ±2%. Values of the ratio of unquenched intensity to quenched intensity, I_o/I, were plotted as a function of quencher concentration. Fits to the general equation $I_o/I = 1 +$ constant [Q] were good. Least squares fitting was used to determine the slopes.

The fluorescence lifetime of 0.8-1.0 x 10^{-3} M (+)-(R)-2-(1-naphthyl)ethyl p-tolyl sulfoxide, 2, in cyclohexane was determined on the Aminco Bowman Spectrophotofluorimeter using the Berlman method (50). The ratio of fluorescence intensities of degassed to undegassed samples was found to be 1.56 ± 0.06. This gives an approximate singlet state lifetime of τ_s = 9.5 ± 1.0 nsec.

Measurements of the lifetime of fluorescence of naphthalene as a function of quencher concentration were performed on a TRW Model 75 A Decay Time Fluorimeter. Excitation light was passed through an interference filter which transmitted 31% at 340.0 nm, 10% at 377.5 nm and 10% at 318.5 nm. Lifetimes were determined by computor simulation of the fluorescence decay curves displayed on a sampling oscilliscope. The values obtained

for an individual sample were reproducible to ±5%. Values of the ratio of unquenched lifetime to quenched lifetime, τ_o/τ, were plotted as a function of quencher concentration. Fits to the general equation $\tau_o/\tau = 1 + \text{constant } [Q]$ were good. Least squares fitting was used to determine the slopes.

The fluorescence lifetime of 0.03 M naphthalene in acetonitrile was determined directly from the emission decay curves several times throughout the course of this study. An average value of $\tau_s = 78 \pm 5$ nsec was obtained.

Measurement of the Inversion Quantum Yield

Solutions for inversion studies were prepared in 10-ml volumetric flasks by the addition of a weighed portion of sulfoxide and an aliquot of a stock solution of naphthalene. Aliquots of exactly 3.0 ml were delivered into each of two preconstricted tubes, and the remainder of the solution was placed in a third tube which was to serve as a blank. The samples were degassed and sealed as above.

Irradiations were carried out in a merry-go-round apparatus which insured equal light absorption by each sample. For irradiations at 313.0 nm a Corning 757 glass filter and a circulating solution filter of 2.38 grams of potassium chromate in 4.5 liters of 1% sodium carbonate were used to isolate the desired line from a 450 watt

medium pressure mercury lamp.

Potassium ferrioxalate actinometry (63) was used to measure light intensities. The literature procedure was modified slightly by the use of stock solutions of ferrioxalate rather than preparing it by precipitation. At 313.0 nm the light intensities were about 3.8×10^{-7} einsteins min^{-1}, and the deviation over the course of irradiation for 72 hours was less than ±3%.

In experiments measuring the kinetics of the naphthalene sensitized inversion of the sulfoxides, the reaction was carried to only 3-6% conversion. Correction for back reaction was made using the following equation, a form of the integrated rate law for approach of the system to stationary state:

$$\beta = 2.303\ \alpha \log[\alpha/(\alpha-\beta')]$$

where β = corrected inversion, α = inversion at the stationary state, i.e., 0.5 for a racemization reaction, and β' = the observed inversion. The observed inversion of the samples was determined by comparing the rotations at the sodium D line of the irradiated solutions and the unirradiated blanks on a Perkin Elmer 141 Polarimeter.

Values of the reciprocal of the quantum yield of inversion, $1/\Phi_{inv}$, were plotted as a function of the reciprocal of the sulfoxide concentration, 1/[S(+)]. Fits to the general equation $1/\Phi_{inv}$ = constant + constant'/

[S(+)] were determined by a least squares method and were usually quite good.

Solutions for the double sensitization experiments were prepared in 10-ml volumetric flasks by the addition of a weighed portion of sulfoxide and an aliquot of a stock solution of benzophenone and naphthalene. Tubes were filled, degassed and sealed as in the inversion studies in the absence of benzophenone.

Irradiations were carried out in a merry-go-round apparatus. Corning 737 and 052 glass filters were used to isolate the 366.0 nm lines from a 450 watt medium pressure mercury lamp. Potassium ferrioxalate actinometry (63) was employed as before. At 366.0 nm the light intensities were about 2.1×10^{-7} einsteins min^{-1}, and the deviation was less than ±2% over the course of irradiation for 6 hours.

The quantum yield of inversion was determined as in the inversion studies in the absence of benzophenone. For samples containing 0.05 M benzophenone, 0.03 M naphthalene and 0.05 M (+)-(R)-methyl p-chlorophenyl sulfoxide, 1c, in acetonitrile the quantum yield of inversion was found to be $\Phi = 0.003 \pm 0.002$. With direct irradiation of naphthalene the quantum yield of inversion is $\Phi = 0.217$. For samples containing 0.05 M benzophenone, 0.03 M naphthalene and 0.05 M (+)-(R)-methyl p-bromophenyl sulfoxide, 1b, in acetonitrile

the quantum yield of inversion was $\Phi = 0.0005 \pm 0.005$. For irradiation at 313.0 nm in the absence of benzophenone the quantum yield of inversion is $\Phi = 0.129$. Irradiation of samples containing 0.05 M benzophenone and 0.03 M naphthalene in acetonitrile under the conditions of the double sensitization studies did not lead to any photoreduction of benzophenone. Comparison of the ultraviolet spectra of the irradiated and unirradiated solutions showed that the concentration of benzophenone was invariant.

A stock solution of 0.011 M (+)-N-acetyl-1-(1-naphthyl)ethyl amine, 3, and 0.094 M (±)-methyl p-bromophenyl sulfoxide, 1b, in acetonitrile was prepared. Aliquots of 3.0 ml were placed in each of 15 tubes which were then degassed and sealed in the usual manner. The tubes were wired to a 450 watt medium pressure lamp equipped with a potassium chromate filter solution having the same characteristics as that used in the 313.0 nm merry-go-round. The output of this apparatus is estimated to be 8×10^{-6} einsteins min^{-1}. The tubes were irradiated for 48 hours. The samples were opened and concentrated to a few milliliters. The sulfoxide was isolated by preparative thin layer chromatography on silica gel and purified by sublimation. The specific rotation of the methyl p-bromophenyl sulfoxide, 1b, measured on the Winkel-Zeiss Polarimeter, was $[\alpha]_D^{25} = 0.0 \pm 0.1$ (c 19.2, chloroform). The irradiated N-acetyl-1-(1-naphthyl)ethyl amine, 3,

isolated and purified by column chromatography on silica gel and unirradiated material had identical specific rotations.

Measurement of the Quantum Yield of Disappearance of Sulfoxide

In the asymmetric induction experiments described above a third component was noted in the preparative thin layer chromatography of the photolysate. The product was isolated but not purified. The nmr and infrared spectra of the crude material were virtually superimposable on those of methyl p-bromophenyl sulfide. No evidence for the formation of methyl p-bromophenyl sulfone was found.

A stock solution of 0.23 M (±)-methyl p-bromophenyl sulfoxide, 1b, and 0.4 M naphthalene in acetonitrile was prepared. Aliquots of 3.0 ml were placed in each of three tubes which were degassed and sealed in the usual manner. The tubes were wired to the lamp and filter apparatus used for the asymmetric induction experiment and irradiated for 48 hours. The tubes were opened and chromatographed on silica gel. Aside from the naphthalene and (±)-methyl p-bromophenyl sulfoxide, 1b, the only product noted was methyl p-bromophenyl sulfide, which was identified by comparison of its infrared spectrum with that of authentic material.

A stock solution of 0.21 M methyl p-bromophenyl

sulfone and 0.4 M naphthalene in acetonitrile was prepared. Aliquots of 3.0 ml were placed in each of three tubes which were degassed and sealed in the usual manner. The tubes were wired to the lamp apparatus used for the asymmetric induction experiment and irradiated for 48 hours. The tubes were opened and chromatographed on silica gel. The recovery of methyl p-bromophenyl sulfone was quantitative.

Stock solutions of varying concentrations of naphthalene and (±)-methyl p-chlorophenyl sulfoxide, 1c, containing 0.005 M hexaethylbenzene in acetonitrile were prepared. For each stock solution aliquots of 3.0 ml were placed in each of 7 tubes which were degassed and sealed in the usual manner. In each set, 3 of the tubes were kept in the dark as blanks. The other tubes were irradiated at 313.0 nm in the merry-go-round apparatus. The light intensity was determined by potassium ferrioxalate actinometry (63) and was found to vary by less than ±3% during irradiation over the course of 72 hours. The samples were opened and analyzed on a Loenco Model 160 Flame Ionization Gas Chromatograph. Separation was effected on a 2 foot column of 10% Carbowax 20 M at a column temperature of 187°. The disappearance of sulfoxide could be determined by comparing the ratios of sulfoxide peak to internal standard peak for the irradiated and blank samples in a given set of tubes.

The results of these experiments are given in Table III.

Table III. Quantum Yield of Disappearance of (±)-Methyl p-Chlorophenyl Sulfoxide

[N]	[S(±)]	$\Phi_{disappearance}$	$\Phi_{racemization}$
0.0192	0.0920	0.0185 ± 0.0073	--
0.0324	0.0916	0.0259 ± 0.0057	0.590
0.0313	0.0450	0.0115 ± 0.0013	0.436

Spectroscopic Studies

Three stock solutions of 0.00297 M naphthalene in acetonitrile, 0.00907 M (±)-methyl p-bromophenyl sulfoxide, 1b, in acetonitrile and 0.00297 M naphthalene and 0.00907 M (±)-methyl p-bromophenyl sulfoxide, 1b, in acetonitrile were prepared. The ultraviolet spectrum of each of the solutions was recorded in the region 245.0-350.0 nm. The spectrum of the mixture was superimposable on the sum of the spectra of the individual components.

Stock solutions of 0.000975 M (+)-(R)-2-(1-naphthyl)ethyl p-tolyl sulfoxide, 2, in cyclohexane and 0.00142 M 1-ethylnaphthalene (J.T. Baker) in cyclohexane were prepared. The ultraviolet spectra of the solutions were taken. The gross structure and positions of the vibrational bands were similar, but differences

existed in the extinction coefficients in the region 330.0-300.0 nm.

Stock solutions of 0.04 M naphthalene, 0.0068 M (+)-(R)-p-tolyl 2-(1-naphthyl)ethyl sulfoxide, 2, and 0.0133 M 1-ethylnaphthalene all in cyclohexane were prepared. The solutions were placed in 13 mm pyrex tubes and were degassed and sealed as usual. The fluorescence spectra were obtained on the Aminco Bowman Spectrophotofluorimeter exciting at 320 nm. The emission spectra of 1-ethylnaphthalene and (+)-(R)-p-tolyl 2-(1-naphthyl)ethyl sulfoxide were virtually identical in position and fine structure. If the quantum yield of fluorescence of naphthalene is $\Phi = 0.29$, then a comparison of emission intensities shows that (+)-(R)-p-tolyl 2-(1-naphthyl)ethyl sulfoxide, 2, has a fluorescence quantum yield of $\Phi = 0.061$.

A stock solution of 0.0012 M (±)-methyl p-bromophenyl sulfoxide, 1b, which had been carefully purified by recrystallization from 5% chloroform--95% toluene, in an ether--alcohol solution (1:2 by volume), was prepared. This solution was placed in a 4 mm quartz tube and was degassed and sealed as usual. The phosphorescence spectrum was obtained at 77°K on the Aminco Bowman Spectrophotofluorimeter exciting at 253.7 nm. The compound showed broad, weak, structureless emission with a maximum at about 405.0 nm.

A stock solution of 1.25 M (±)-methyl p-bromophenyl

sulfoxide, 1b, which had been carefully purified by recrystallization from 5% chloroform--95% toluene, sublimation at 70°/0.05 mm, zone melting at 85° (10 passes with 11 zones/pass) and resublimation at 70°/0.05 mm, in chloroform was prepared. The solution was placed in a 10.0 cm cell and the absorption spectrum was obtained on the Cary 14 Recording Spectrophotometer. The approximate positions and extinction coefficients of the vibrational fine structure of the singlet-triplet absorption spectrum are given in Table IV.

Table IV. Singlet-Triplet Absorption Spectrum of (±)-Methyl p-Bromophenyl Sulfoxide

λ_{sh} (nm)	ε
365.8	0.026
353.0	0.061
342.4	0.083
332.8	0.094

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PROPOSITION I

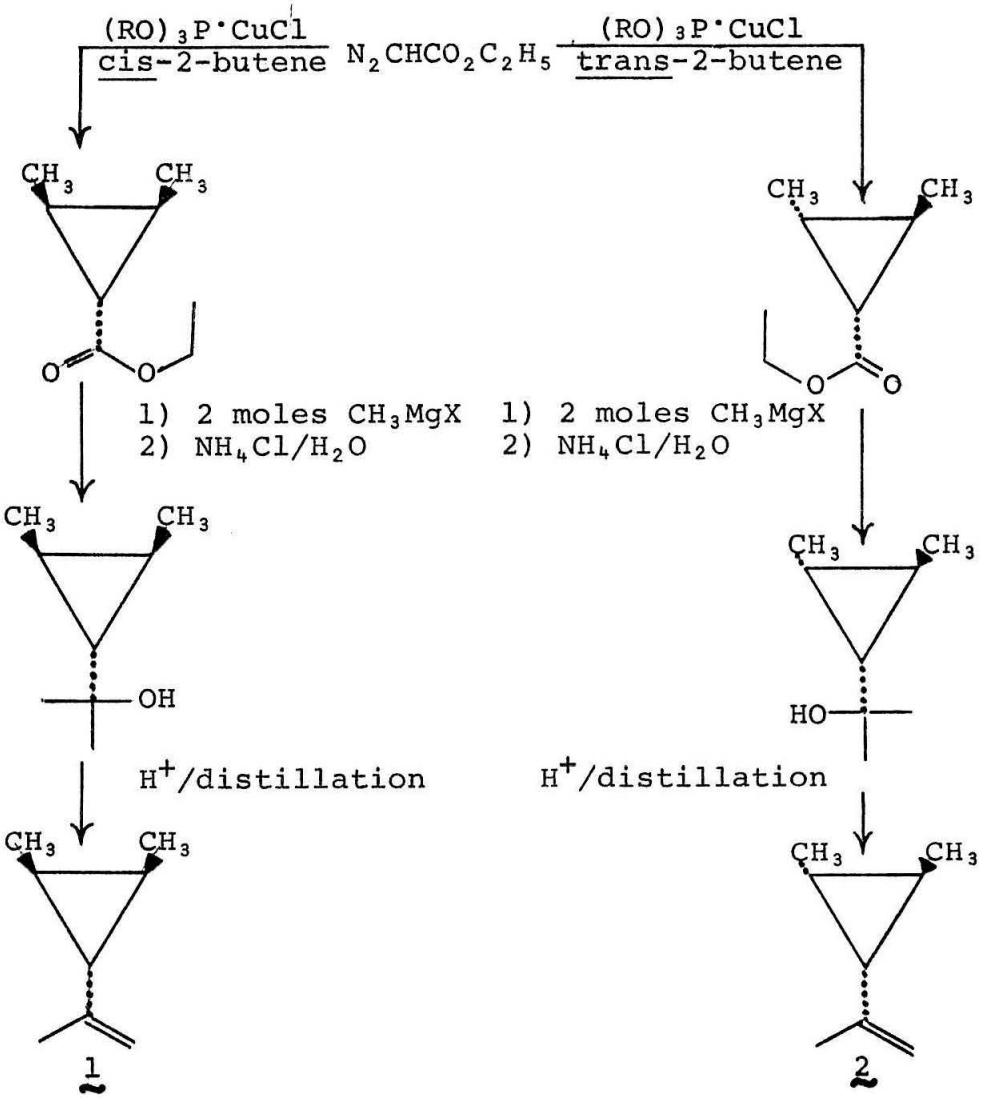
It is proposed that a study of the stereochemical consequences of the photochemical vinylcyclopropane-cyclopentene rearrangement be undertaken. Such an investigation would permit differentiation between a mechanism involving a diradical intermediate and one which is an allowed suprafacial [1,3]-sigmatropic shift.

The photochemistry of vinylcyclopropanes is of interest in view of the prediction (1) that the rearrangement to cyclopentenes may occur as a suprafacial [1,3]-sigmatropic shift in the first excited singlet state. In previous studies (2, 3, 4, 5) the presence of other chromophoric units complicates the situation by introducing excited singlet states at lower energy than that of the vinylcyclopropane. It has recently been shown in our laboratories (6) that in the photorearrangement of isopropenylcyclopropane to 1-methylcyclopentene the prediction of facile conversion from an excited singlet state is in fact correct.

Two pathways for this rearrangement are immediately obvious. The excited singlet molecule may undergo cleavage of one of the cyclopropane bonds to give a diradical which may reclose to starting material or form the cyclopentene. On the other hand, the reaction may proceed in a concerted manner by way of a suprafacial [1,3]-sigmatropic shift.

A choice between these two mechanisms can be made by studying the rearrangements of trans, trans-2,3-dimethylisopropenylcyclopropane, 1, and cis, trans-2,3-dimethylisopropenylcyclopropane, 2. These compounds may be synthesized as shown in Scheme I. The use of (trialkyl phosphite) copper (I) chloride complexes to catalyze the

Scheme I



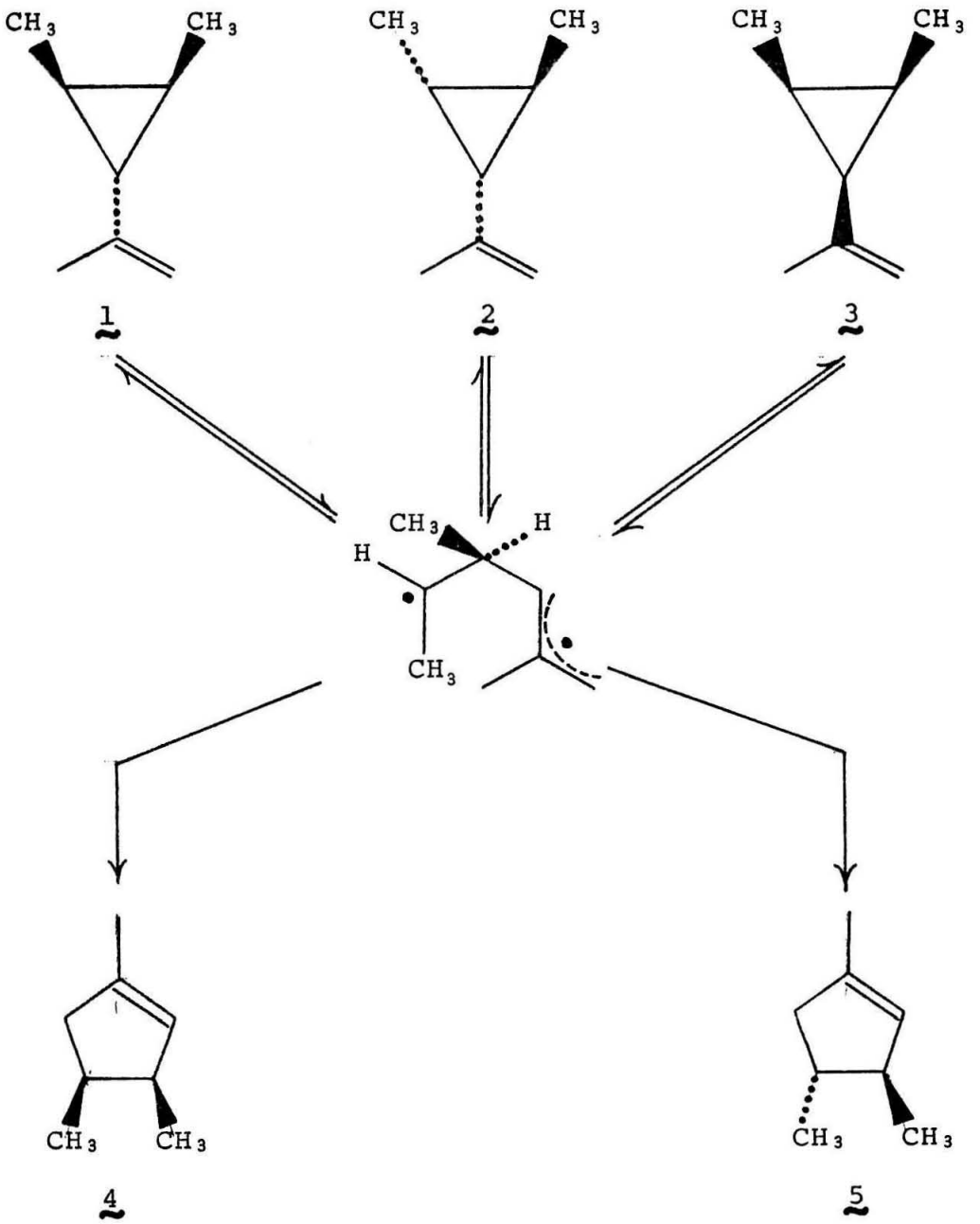
addition of ethyl diazoacetate to olefins has been studied by Moser (7, 8). The acid catalyzed dehydration of tertiary cyclopropylcarbinols has been demonstrated by Volkenburgh et al. (9) in the conversion of methyl cyclopropyl ketone to isopropenylcyclopropane.

If the photorearrangement proceeds through a diradical intermediate, the mechanism may be represented as shown in Scheme II. Under these conditions both cis-3,4-dimethyl-1-methylcyclopentene, 4, and trans-3,4-dimethyl-1-methylcyclopentene, 5, are expected as products. Furthermore, interconversion of the three 2,3-dimethyl-isopropenylcyclopropanes, 1, 2 and 3, will be observed.

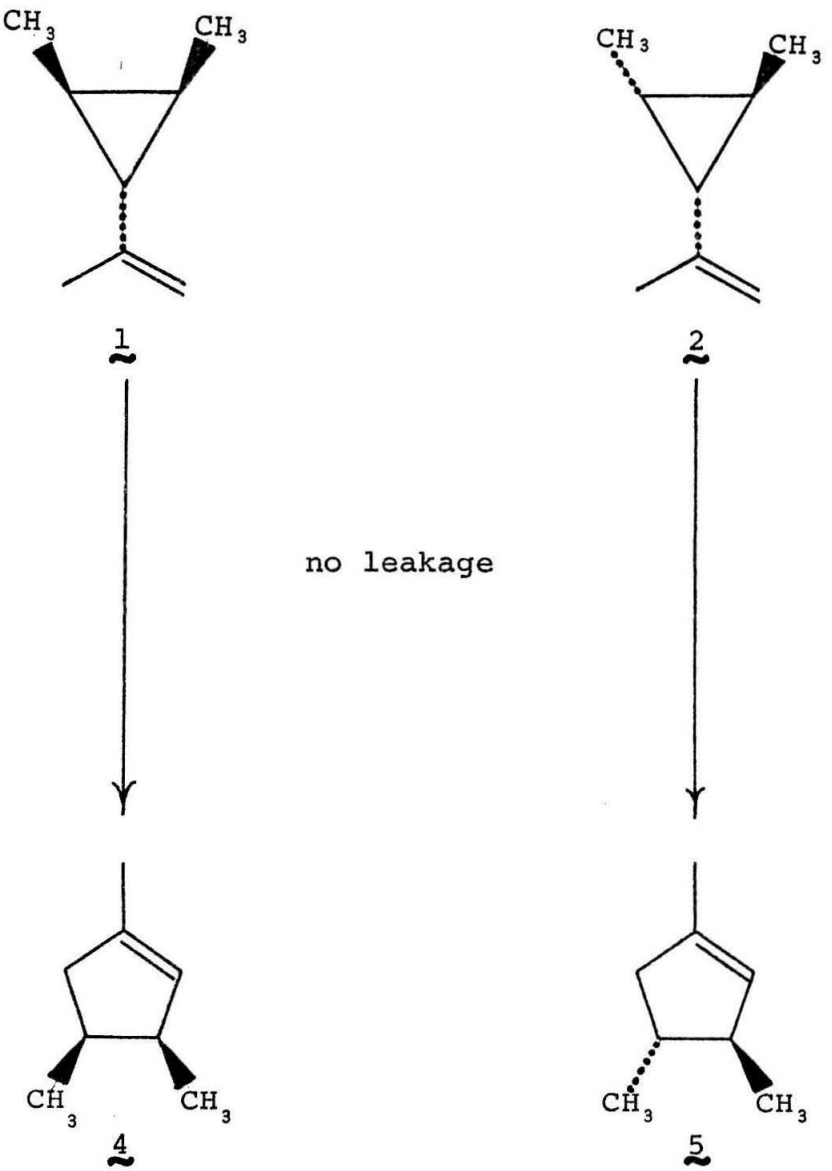
If the photorearrangement proceeds through a suprafacial [1,3]-sigmatropic shift, the mechanism may be represented as shown in Scheme III. Here no scrambling of starting material occurs, and trans, trans-2,3-dimethyl-isopropenylcyclopropane, 1, gives only cis-3,4-dimethyl-1-methylcyclopentene, 4, while cis, trans-2,3-dimethyl-isopropenylcyclopropane, 2, gives trans-3,4-dimethyl-1-methylcyclopentene, 5.

Casual observation of the number of products obtained will strongly support one or the other of the schemes. Definite proof of the mechanism will require separation and identification of the photoreaction components.

Scheme II



Scheme III



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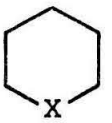
PROPOSITION II

A nuclear magnetic resonance study of the ring flipping process in a series of perinaphthanes is proposed.

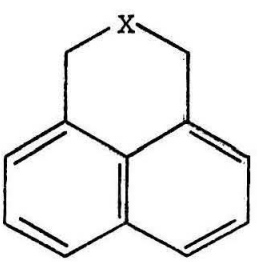
A number of studies of the ring flipping process in six-membered carbocyclic compounds have been undertaken. Anet and coworkers (1) and Bovey and coworkers (2) independently studied the undecadeuterocyclohexane system and obtained the values $\Delta H^{\ddagger} = 10.7$ kcal mole^{-1} and $\Delta S^{\ddagger} = 2.0$ eu for this process. Hendrickson (3) has suggested that this inversion process involves a transition state in which four carbon atoms are coplanar. Anet and Haq (4) have also studied the cyclohexene-3,3,4,5,6,6-d_6 system which exists in a half chair configuration. They obtained the values $\Delta H^{\ddagger} = 5.3$ kcal mole^{-1} and $\Delta S^{\ddagger} = 1.3$ eu (calculated) for the activation parameters. In this ring flipping process a transition state is suggested in which five carbon atoms are coplanar.

Lambert and Keske (5) have studied a number of six-membered cyclic compounds containing five carbon atoms and one heteroatom. Their results are given in Table I.

Table I. Rate Parameters for 

X	Solvent	T_c	E_a (kcal mole^{-1})
SO	CH_2Cl_2	-70	14.2
SO_2	CH_2Cl_2	-63	14.9
S	CH_2Cl_2	-93	11.6
O	CD_3OD	-80	10.7
NH	CD_3OD	-63	14.5
CH_2 (1)			11.3

A study of the ring flipping processes in the peri-naphthane derivatives 1a - 1e is of interest for two reasons. First, the six-membered ring is constrained by the naphthalene system so that it may possibly require



1

a X = S

b X = SO_2

c X = O

d X = CD_2

e X = $C(CH_3)_2$

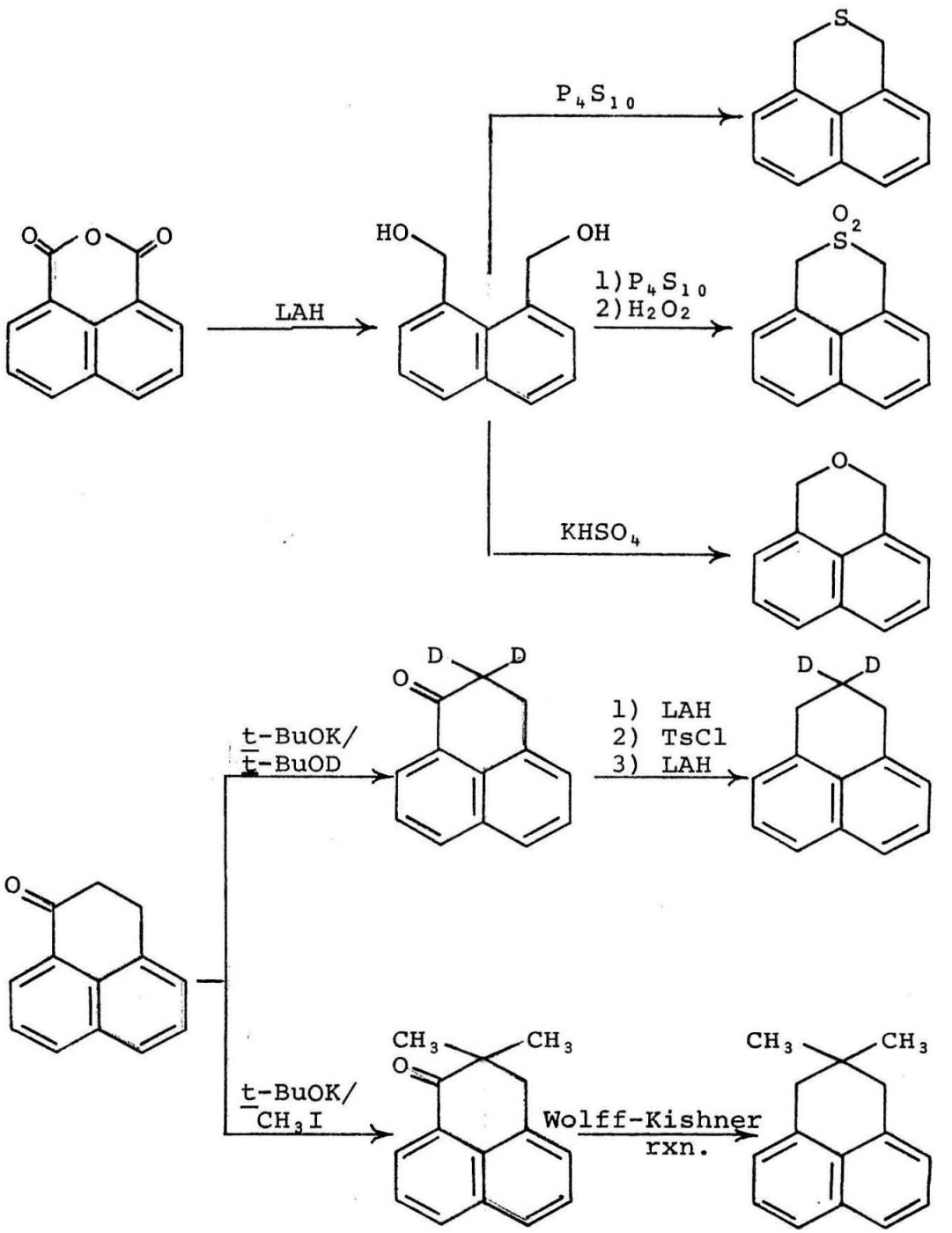
a transition state for inversion with all six atoms coplanar. Second, the effects of substituting a heteroatom for a methylene group may be easily investigated.

These perinaphthanes are expected to have the X-grouping out of the plane of the rest of the molecule. Certain distortions of the naphthalene system will be present, but in the case of 1,8-dimethyl-3-bromonaphthalene (6) these have been shown to be in-plane deformations (about 4°) of the methyl groups. A ring flipping transition state with all atoms coplanar is expected, although others may be possible.

Studies such as those done by Lambert (5) indicate that substitution of an oxygen atom for a methylene in a six-membered ring lowers the barrier for inversion, while substitution of nitrogen or sulfur tends to raise it. No explanation of these results is given. Since the activation energy involved in ring flipping may result from angle deformations, the C-N-C and C-S-C bonds may be less readily bent than the C-C-C bonds, and the C-O-C bonds may be the most readily deformed. In this study the generality of this effect could be demonstrated.

The syntheses of compounds 1a - 1e are straightforward and are shown in Scheme I. The synthesis of 2-oxaperinaphthane, 1c (7, 8), 2-thioperinaphthane, 1a (9), and 2-thioperinaphthane dioxide, 1b (9), have been described by other workers. The synthesis of

Scheme I


LAH
HO
OH
P_4S_{10}
1) P_4S_{10}
2) H_2O_2
$KHSO_4$
t-BuOK/
t-BuOD
D
D
1) LAH
2) TsCl
3) LAH
t-BuOK/
CH_3I
CH_3
CH_3
Wolff-Kishner
rxn.

perinaphthane-2,2-d_2, 1d, and 2,2-dimethyl-perinaphthane, 1e, depend on 1-perinaphthanone (10) as a key intermediate. Exchange or methylation at the 2-position should be straightforward. The ketone group may be removed in a Wolff-Kishner reduction or by lithium aluminum hydride reduction of the tosylate.

A study similar to the one proposed has been carried out by Anderson and Oehlschlager (11) who studied the ring flipping in some 2-alkyl-2,3-dihydro-1H-benz[d,e]isoquinolines. They observed coalescence temperatures around -60°. The coupling of the methylene protons to those of the naphthalene ring, the nitrogen methyl group or to the other methylene group broadened the AB pattern but did not interfere with activation parameter analysis. Their work is complicated by the presence of the nitrogen inversion process as well as the ring flipping. The authors feel that the pyramidal inversion of nitrogen is rate-limiting in this strained system. Comparison of their activation energies with the trend for other heteroatom substitution should shed light on this unusual suggestion.

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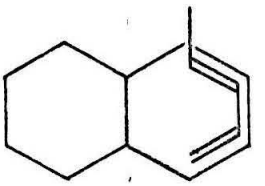
PROPOSITION III

It is proposed that the compounds cis- and trans-2,3-dimethyl-8-(1-naphthyl)octa-2,4-diene be synthesized and used as probes of the configuration of the exciplex formed in the quenching of the naphthalene singlet state by conjugated dienes (1).

Recent work by Hammond and coworkers (2, 3, 4, 5, 6) has shown that the excited singlet state of naphthalene and certain other aromatic hydrocarbons may be quenched by conjugated dienes. Although there is no direct evidence for such a species, the mechanism for this process has been explained in terms of an excited complex, or exciplex. The complex is formed from an excited naphthalene molecule and a ground state diene molecule. The exciplex then appears to undergo rapid radiationless decay to the ground states of both molecules with no observable reaction.

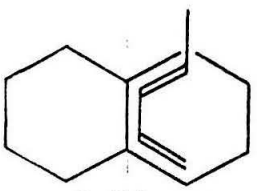
Salem (7) has performed theoretical calculations on these exciplex systems using his intermolecular orbital theory of the interaction between conjugated systems. His results indicate that configurations $\underset{\sim}{1}$ - $\underset{\sim}{5}$ lead to the greatest stabilization energy and should be most important in exciplex formation. Of these, configurations $\underset{\sim}{1}$ - $\underset{\sim}{4}$ have the diene and naphthalene in parallel planes, that is, the "face to face interaction" commonly accepted

for excimer formation. Configuration 5 places the diene and naphthalene molecules in perpendicular planes which intersect at the bond between C_9 and C_{10} of the naphthalene species. This configuration has been referred to as the "cradle interaction".



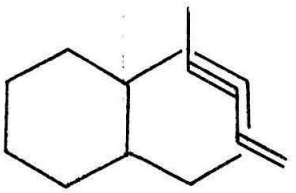
0.64 ev

1



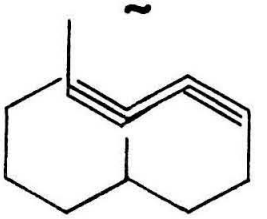
0.34 ev

2



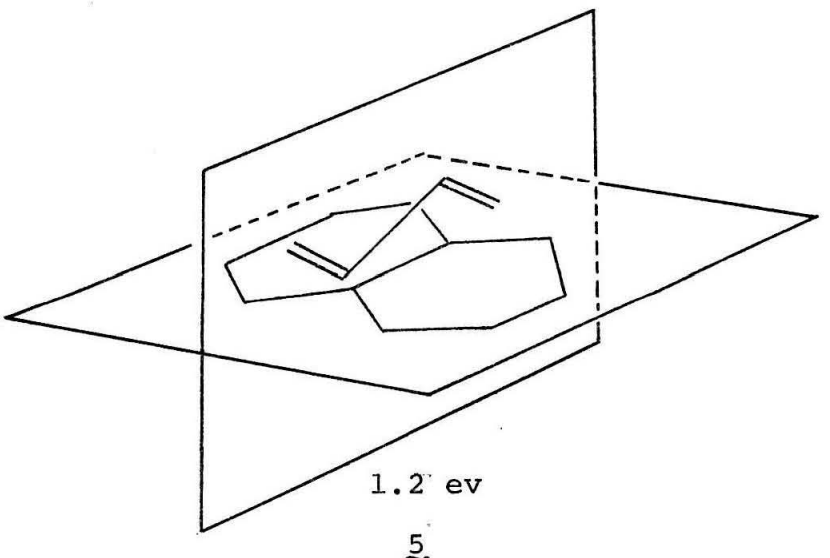
0.80 ev

3



0.36 ev

4



1.2 ev

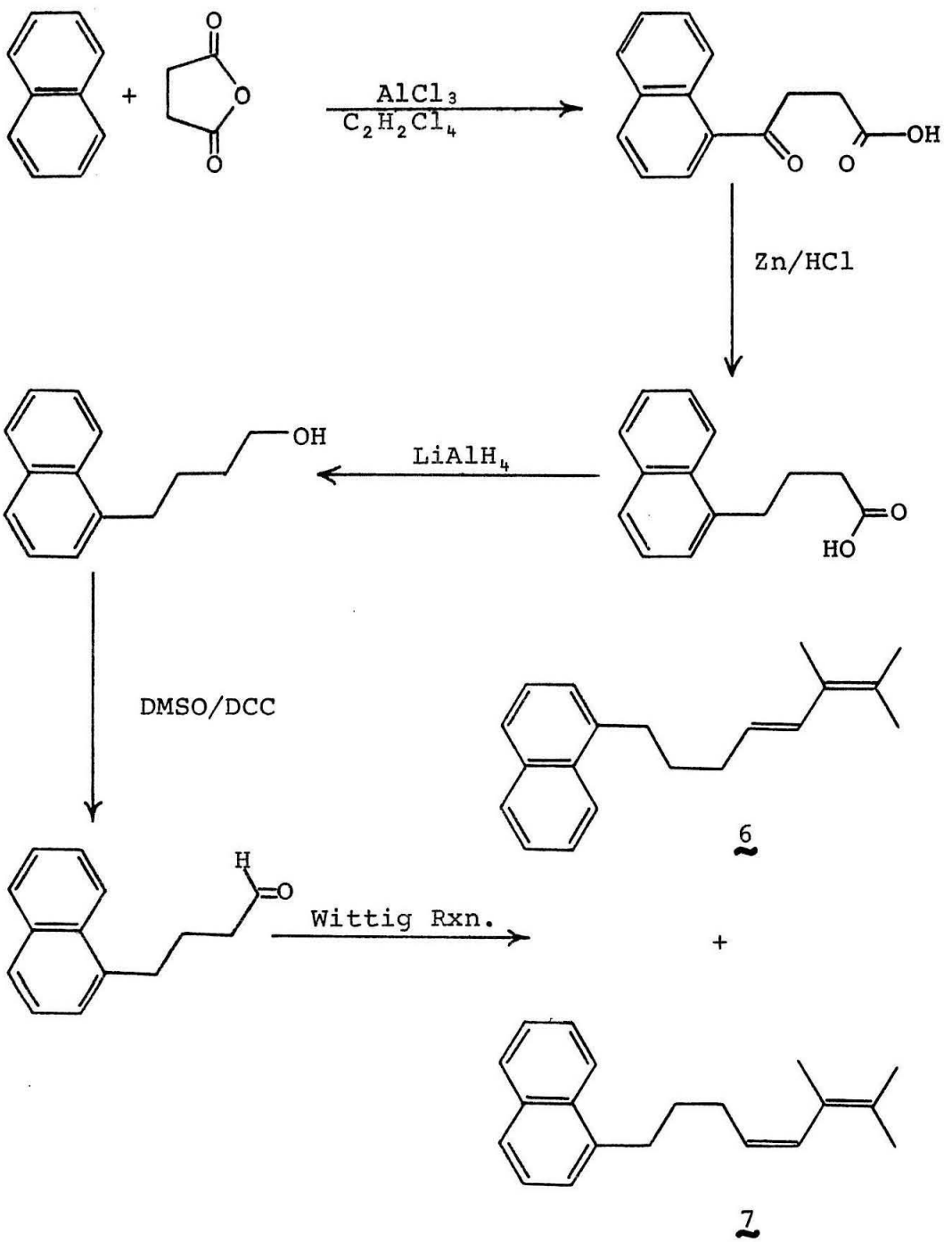
5

The proposed investigation will give experimental evidence differentiating between the "face to face" and "cradle" interactions.

The proposed synthesis of trans-2,3-dimethyl-8-(1-naphthyl)octa-2,4-diene, 6, and the cis diene, 7, are shown in Scheme I.

A very strong directing effect is exerted by the solvent in Friedel-Crafts reactions on naphthalene. With acetyl chloride in tetrachloroethane the product is 93% 1-acetylnaphthalene (8). The use of succinic anhydride in Friedel-Crafts acylations has been demonstrated by Somerville and Allen (9). Precedent for the zinc reduction of the aromatic ketone has been given by Martin (10). Reduction of the acid to an alcohol and subsequent oxidation to an aldehyde are well known reactions (11). The salt required for the Wittig reaction with 4-(1-naphthyl)butanal may be prepared by allylic bromination of tetramethylethylene (12) and reaction with triphenyl phosphine. The Wittig reaction itself is usually rather non-stereospecific. Lithium bromide or iodide has been used with considerable success to yield cis olefins (13). Separation of cis and trans isomers of the final product should be possible either by preparative vapor phase chromatography or by column chromatography on silver nitrate impregnated material.

Scheme I



6

7

Examination of molecular models shows that the trans diene, 6, can readily assume configurations 1 - 3 while the cis diene, 7, can only assume configuration 4. Neither compound can achieve optimal geometry in the "cradle interaction", 5, but in both compounds considerable stabilization is possible.

If the "face to face interaction" is operating, 6 should show considerable exciplex formation while compound 7 should show much less. If the "cradle interaction" is operating both compounds will show about the same amount of exciplex formation. Since exciplex formation is one means of deactivating the singlet state of naphthalene, its importance will be reflected in the singlet lifetimes of compounds 6 and 7. These may be determined readily using the method of Berlman (14) or directly from the fluorescence decay curves.

Although not of prime concern in this proposal, the photochemistry of compounds 6 and 7 would be of considerable interest. A standard survey of these reactions could be undertaken.

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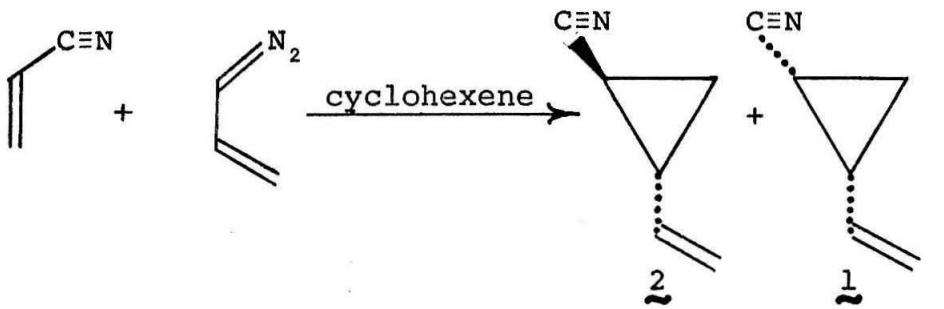
PROPOSITION IV

It is proposed that the vapor phase thermal rearrangement(s) of cis-cyano-vinylcyclopropane, 1, and trans-cyano-vinylcyclopropane, 2, be investigated.

A number of studies of thermal rearrangements of vinylcyclopropanes have been undertaken (1). The pathways available to these compounds may be rationalized in terms of a mechanism involving a 1,3-diradical. Substitution of the cyclopropane ring with another vinyl group (2,3) or an ethynyl group makes available other pathways, and more recently a deep-seated rearrangement of diethynylcyclopropane has been observed (4). The proposed study would investigate the rearrangement(s) in compounds where the cyclopropyl ring contains both vinyl and cyano substituents.

The synthesis of cis- and trans-cyano-vinylcyclopropane is shown in Scheme I. The procedure (5) is simple but requires the separation of the two isomers.

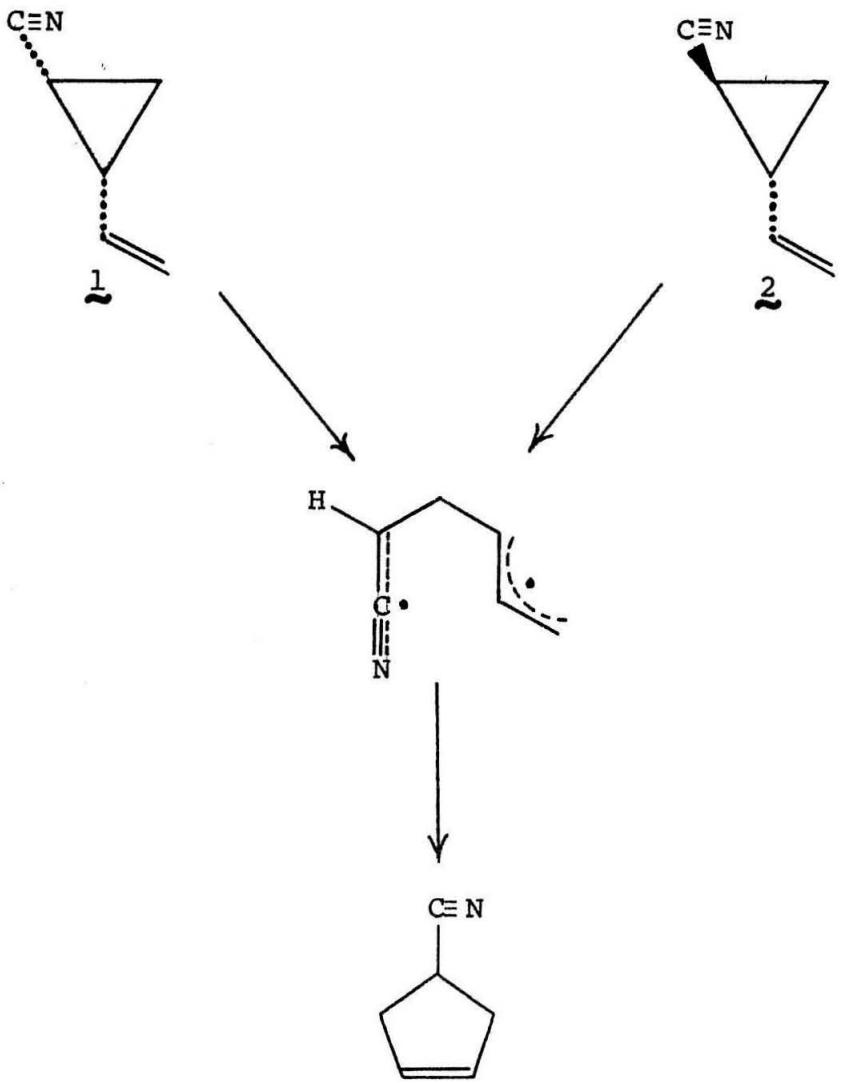
Scheme I



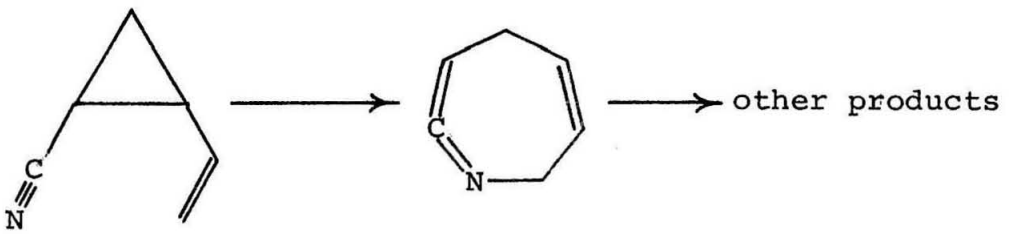
A number of possible rearrangements may be envisioned for these compounds. Three such possibilities are shown below. The division into these mechanisms is admittedly artificial. However, all of these suggestions are reasonable, especially since a heteroatom is present, and it is difficult to predict which of the schemes will predominate.

Initial studies will be carried out in a flow system with nitrogen as the carrier gas. This will permit isolation of amounts of products sufficient for identification. Kinetic runs and activation parameter analyses will be made in a static reactor.

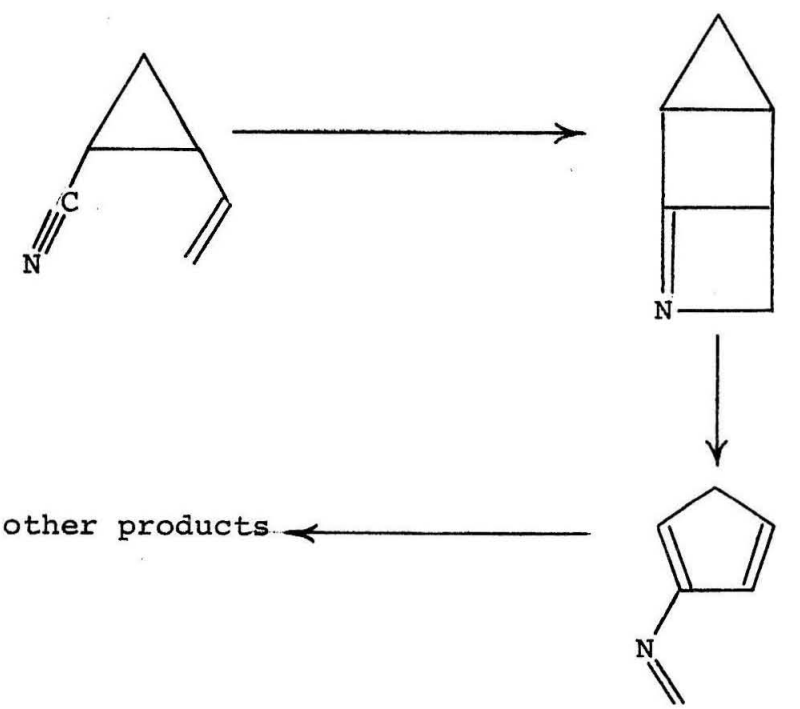
Scheme II



Scheme III



Scheme IV



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PROPOSITION V

It is proposed that azo-(cis-2-butene) and azo-(trans-2-butene) be synthesized for free radical studies in which the rate of cis-trans isomerization of allylic radicals can be obtained (1).

A number of studies of the conformational stability of the allylic radical have been undertaken. Walling and Thaler (2) studied the allylic chlorination of olefins using t-butyl hypochlorite in a photoinitiated reaction. They found that if they started with a pure cis or trans olefin that considerable stereoselectivity was shown. In the case of the 2-butenes complete stereospecificity was shown at temperatures as high as 40°, but to maintain this selectivity in the case of the 4,4-dimethyl-2-pentenes it was necessary to run the reaction at -78°. Thaler et al. (3) studied the addition of thiols to piperylenes with and without added oxygen. In the case of 1,2-addition, where a thiyl radical adds to the terminal methylene and the resulting allylic radical is trapped in the 2-position by oxygen or thiol to form a vic-thiol hydroperoxide or a simple thiol, the stereochemistry of the products can be used as a measure of the conformational stability of the allylic radical. In the case of benzene thiol with oxygen present, greater than 99% retention of stereochemistry was observed.

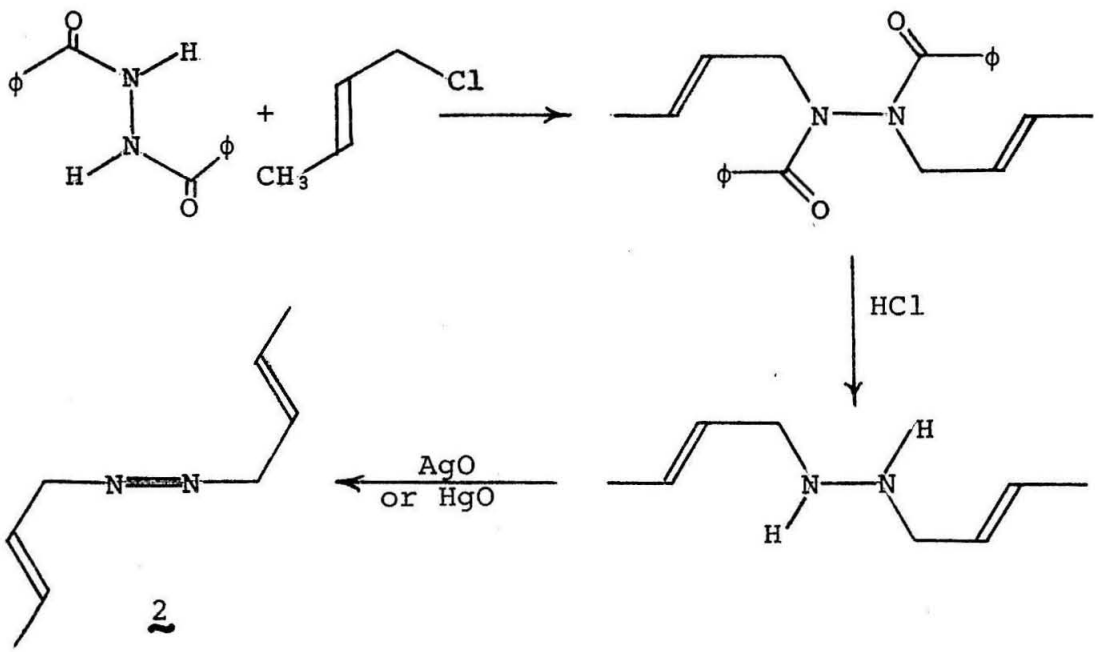
With benzene thiol in degassed solutions, greater than 92% retention was observed, but with methane thiol in degassed solution little or no retention was observed. Denney et al. (4) have studied the reduction of allylic chlorides using triphenyltin hydride. They find that at 80° starting with either cis- or trans-1-chloro-2-butene that the composition of the resulting 2-butenes is the same. Neumann et al. (5) have found that the addition of triphenyl- and trimethyltin radicals to piperylenes is reversible and that when there is an excess of diene present the recovered material is between 3% and 55% isomerized. Recently Krusic and Kochi (6) have generated cis- and trans-methallyl radical in an esr cavity by photolysis of cis- and trans-2-butene in the presence of t-butyl peroxide. Little isomerization was observed at temperatures up to 0°.

It seems clear from these studies that the allylic radical does isomerize, but that there is a considerable (perhaps 13 kcal $mole^{-1}$) activation energy for this process. Since absolute rate constants are difficult to obtain in radical reactions, the rates of isomerization have never been measured, and this barrier is not known.

The proposed determination of the rate constants for the cis-trans isomerization requires the synthesis of azo-(cis-2-butene), 1, and azo-(trans-2-butene), 2. The best method of preparing symmetrical alkyl azo

compounds is from the corresponding sym-dialkyl hydrazine (7, 8). However, these sym-dialkyl hydrazines cannot be prepared in reasonable yield by simple alkylation of hydrazine (9, 10) unless diformyl or dibenzoyl hydrazine is used to prevent further alkylation (11). The most promising synthesis of these compounds is shown for azo-(trans-2-butene) in Scheme I. The method for preparing the cis- compound is analogous.

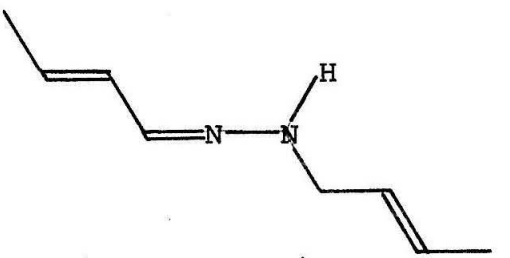
Scheme I



The procedure to the hydrazine is similar to that of Hatt (11) and requires the use of either trans- or

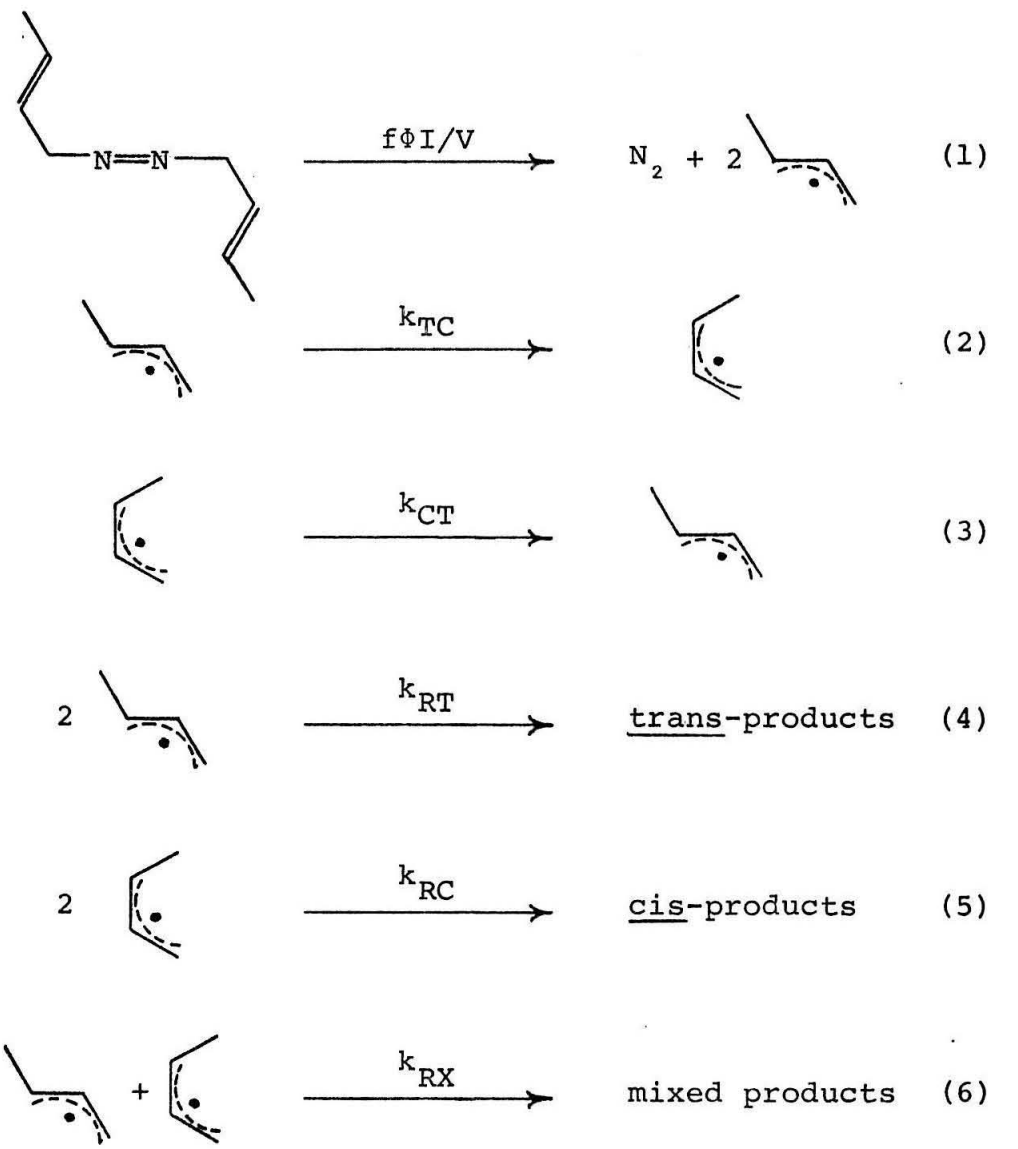
cis- crotyl chloride (12). The oxidation to the azo compound may be effected in a number of ways. Blackham and Eatough (8) and Renaud and Leitch (13) have used mercuric oxide with considerable success. Chaco and Rabjohn (7) prefer silver oxide. These oxidations are mild and are performed under neutral conditions.

It should be noted that azo-(trans-2-butene) is expected to be somewhat unstable. Thermal decomposition should occur at moderate temperatures and the acid or base catalyzed tautomerization to hydrazone 3 should be facile. However, mixtures of the hydrazone and azo compounds can be converted in high yield to pure azo compound using the tautomerization procedure of Ioffe et al. (14).



3

The photochemical decomposition of azo-(trans-2-butene) is shown in equations 1-6. The mechanism for the cis- compound is completely analogous and will not be discussed.



(1) (2) (3) (4) (5) (6)

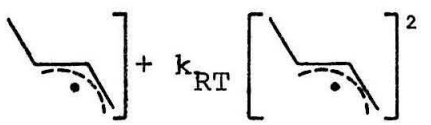
Even if no isomerization occurs upon cage recombination, the kinetic law for this mechanism is an extremely complex expression. To simplify this equation such that experimental results are easily interpretable,

it is proposed that the reaction be run under conditions where only a very small amount of cis- products are formed. Such conditions allow one to make the following assumptions;

1. Step 3 is not important since the concentration of cis-radicals is small with respect to trans-radicals and k_{CT} is probably of the same magnitude as k_{TC}.
2. Step 5 is not important since it depends on the square of the cis-radical concentration.

Step 6 will be the only important process for removing cis-radicals assuming that $k_{RX}[t\text{-}C_4H_7\cdot]$ is much greater than k_{CT}. These assumptions lead to the kinetic expression shown below. The quantum yield for decomposition can be

$$f\Phi I/V = k_{TC}\left[\quad\right] + k_{RT}\left[\quad\right]^2$$



determined from simple photochemical experiments. The value of f may be determined by intercepting all the radicals which diffuse out of the solvent cage. The values of I and V will be known quantities under the experimental conditions. The concentration of trans-allylic radicals will be approximately equal to the total

radical concentration which is determined from the intensity of the esr signal. The value of k_{RT} is the second order rate constant for radical recombination and is obtainable using the techniques developed by Weiner and Hammond (15). Therefore, from the kinetic expression an approximate value of k_{TC} is obtainable.

Experimentally a number of problems still remain. The products of the reaction must be separated and identified. These products could be dimers or the products from disproportionation, but in either case they will reflect the stereochemistry of the radicals from which they were formed. Conditions must be found where little cis-product is formed. With variation of the light intensity to change the steady state radical concentration and variation of temperature to effect the value of k_{TC} it should be possible to find such conditions. Once conditions for the determination of the rate of cis-trans isomerization have been found, an activation parameter analysis should be possible.

Although the determination of the conformational stability of the allylic radical is of first concern in this proposal, the availability of a clean source of allylic radicals suggests other studies such as the determination of rate constants for hydrogen abstraction from various donors. Since the radical is a reasonably stable one, the spread of these values is expected to be large.

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